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THE PHOTO EFFECT IN SILVER-OXYGEN-CESIUM PHOTOCATHODES

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THE PHOTO EFFECT IN SILVER-OXYGEN-CESIUM PHOTOCATHODES

P. G. Borzyak

Summary

The author has investigated the photo effect, in relation to the optical properties, of dispersed films of silver coated with adsorbed films of cesium, complex oxygen-cesium films, and films of cesium oxide. The results of his experiments lead to the conclusion that the photo effect of the silver particles in a silver-oxygen-cesium cathode plays an important, and occasionally the principal role in the photoelectric emission of such cathodes.

Introduction

Modern photocells use mainly two types of photocathode: antimony-cesium (Sb-Cs) and silver-oxygen-cesium (Ag-O-Cs). Our knowledge of the principal properties of the Sb-Cs cathode is based on more or less clearly defined physical concepts -- according to the present theory it is a semiconductor, the intense photo effect of which is due to the photoelectric nature of the intrinsic optical absorption. This is also reflected in a certain parallelism between the spectral characteristics of the photo effect and optical absorption of Sb-Cs cathodes.

Our ideas concerning the fairly lengthy history of the Ag-O-Cs cathode are more confused. It is widely considered that in this case the sources of photoelectrons are atoms of cesium adsorbed on the oxide, while, an "intermediate" layer between the backing and the film of adsorbed cesium, the cesium oxide plays an auxiliary role. On the other hand, it has recently been suggested that the Ag-O-Cs cathode may be a cathode of the semiconductor type. This, of course, postulates a bulk type of photo effect, and the role of the surface film of adsorbed cesium is seen as consisting mainly in the reduction of the electron work function. Stressing the semiconductor nature of the photocathode also implies that the grains of metal deposited in the film, when the silver oxide is reduced with cesium, are a secondary (as far as the photo effect is concerned) product of the technological process, i.e., a neutral impurity in the cathode. This view attributes importance only to atomic metal impurities in the cesium oxide lattice, which create local electron levels with a reduced dissociation energy, leading to an improvement in the conductivity of the cesium oxide and possibly to the appearance of additional centers of photoelectric emission.

Sometimes, without regard to the mechanism, it is said that the cesium content is responsible for the photo effect in one (the longwave) region of the spectrum and the silver content in the other (shortwave).

As early as 1935, Lukirskiy and Khurgin [1] expressed the idea that the photoelectric emission from an Ag-O-Cs cathode is, in fact, emission from colloidal particles of silver buried in the cesium oxide. Apart from Soviet authors, certain foreign scientists [2] have recently expressed similar opinions.

Finally, in one of the most recent papers on this subject, presented at the Kiev conference on cathode electronics, Yumatov [3] suggests that in the longwave region of spectral sensitivity of an Ag-O-Cs cathode the photo effect is linked with the cesium atoms adsorbed on the cesium oxide (ad-atoms), and in the shortwave region with the cesium filling the capillaries between the individual cathode crystals. In Yumatov's scheme the silver particles are again neutral in relation to the primary photo effect.

Thus, there is no generally accepted theory of the physics of the Ag-O-Cs

photocathode, and in particular directly contradictory views are held concerning the role of metal particles of the colloidal type in such cathode films. Repeated attempts by various authors to seek the aid of data on the optical properties of photocathodes and establish some kind of relationship between the spectral characteristics of the photo effect and the optical absorption have proved unsuccessful. In these cases, measurements have been made primarily of the reflection, and sometimes of the transmission, and conclusions of a qualitative nature have been drawn concerning the absorption of light within the total thickness of the cathode.

We made the measurements needed to determine all three coefficients: reflection R, transmission D, and absorption A, on thin-film photocathodes with a thickness of the order of the effective thickness, which follows from the relations between the photocurrents corresponding to direct and back illumination. At the same time, we registered the spectral characteristics of the photo effect. By way of example, Fig. 1 shows the data obtained for an industrial type of thin-film photocathode illuminated from the back. From these data it is clear that there is no correspondence between the spectral characteristics of the photo effect and the absorption of light, even for the effective thickness. The same result was also obtained for effective-thickness sections of the cathodes we had studied previously [4].

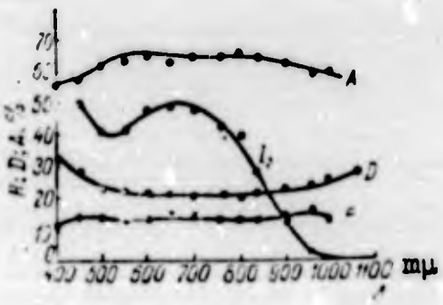

Fig. 1.

The problem of the Ag-O-Cs cathode and the principal factors determining its photoelectric properties remained unsolved, and we therefore decided to investigate this question by some cathode modeling technique. In our previous investigations of the Ag-O-Cs cathode, characterized by a macroscopic approach [4] and also involving the determination of the effective thickness, we were engaged mainly in clarifying the part played by optical factors in the photo effect. In this connection, we determined the optical constants giving the general optical characteristic. In the investigations described here we elucidated the role of the structural elements of the Ag-O-Cs cathode. If, from the point of view of mechanical structure, the cathode is a mixture of commensurable quantities of crystallites of silver and cesium oxide, the surface of the cathode can not consist of a single, continuous, even though loose film of cesium oxide. This surface must consist of alternating patches of silver and cesium oxide, coated, of course, with the active films that reduce the electron work function. In a thin-film photocathode the mixed particles of metal and cesium oxide must exist in some simple formation of the two-dimensional type. It is natural to inquire whether the observed photoelectric emission is additively composed of two components: the emissions of the metallic and oxide fractions of the photocathode, or whether one of these structural elements of the cathode has no relation to its electron-emission properties.

In order to solve this problem, it is possible to isolate one of the components of the cathode, study its properties and thus determine its part in the general Ag-O-Cs photocathode effect. We have in mind a study of the photo effect of the system Ag-Cs. At first glance, this may appear unnecessary, since the photo effect corresponding to a system consisting of a silver backing with adsorbed films of alkali metals has already been thoroughly investigated. This, however, relates to a massive, continuous silver mirror. If we wish to simulate the silver component of an Ag-O-Cs cathode, on the one hand, or the cathode itself, on the other, we must think in terms of dispersed films of silver, consisting of individual grains, possibly only partially in contact with each other. This would represent the metal

skeleton of an Ag-O-Cs cathode, at least a thin-film one, from which the cesium oxide had been removed. Such a film, for example, would have optical properties quite different from those of a continuous film of silver. Apart from the problem of the Ag-O-Cs cathode, a study of the photo effect of finely dispersed particles of silver holds considerable independent interest, and we shall consider this point in some detail. After studying such a cathode model, we can complicate it further by creating on the silver particles adsorption films of a complex type and then by covering them with cesium oxide, as in the Lukirskiy-Khurgin model. We have attempted to perform a series of experiments of this kind.

The Photo Effect of Mosaic Films of Silver Coated with Adsorbed Films of Cesium

The investigations were carried out on silver films of variable thickness, condensed from the vapor onto a glass backing. In the region of small "thicknesses" these metal films display a number of anomalies connected with the fact that they cease to be continuous and acquire a granular, mosaic structure [5]. The characteristics of silver films of variable thickness have recently been carefully investigated by Morozov and Butslov [6] and other authors [7]. Our own photoelectric investigations were preceded by a repetition of the previous experiments of other authors on the optical characteristics of the films investigated. A typical example of the results obtained is illustrated in Fig. 2, which shows the distribution over a silver film of variable thickness of the coefficients of reflection R, transmission D and absorption A = 1 - (R + D), determined from the experimental data, for light with wavelengths of 450 and 800 mμ. The abscissas represent distances along the film measured in mm from an arbitrarily selected point.

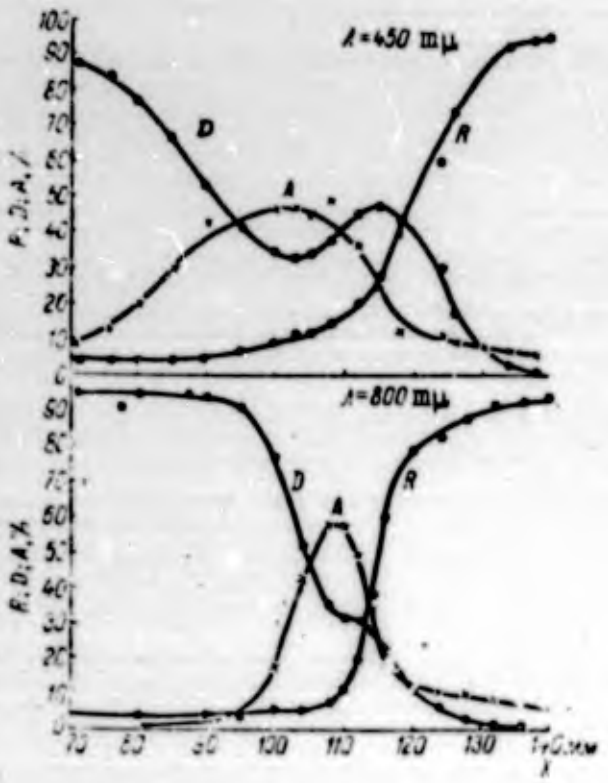

Fig. 2.

Note the following interesting aspects of the optical characteristics of such films. In the region where the film has a granular structure, it also hardly scatters the light [7] and behaves like a continuous film with mirror reflection; all the transmitted light is concentrated in a straight beam.

The uniqueness of the optical properties of these films consists in the fact that there is not the ordinary correspondence between the characteristics of transmission D(x) and reflection R(x). For example, within a definite interval of "thicknesses" an increase in reflection is also accompanied by an increase in transmission. Particularly interesting are the absorption characteristics (as functions of the film thickness) which form curves with maxima corresponding to extremely high values of A. Fig. 3 shows a family of A(x) curves for different wavelengths, obtained for a film to which the data of Fig. 2 also apply. Of course, the presence of high optical absorption within a certain region of film thicknesses is also of interest in relation to the possibility of using it for the photo effect.

In order to study the photo effect in the visible region of the spectrum, we

coated a film of silver with an ad-film of cesium, which was introduced into the tube through an inlet by breaking an ampoule in a branch of the tube. Fig. 4 shows the distribution of the photocurrent over the film I(x) for an approximately optimal amount of cesium. Curve 1 is for a film of silver on a glass backing, curve 2 for a film on an adjacent strip of platinized glass. The distribution for the glass backing is typical. This was verified on different tubes under different conditions of introduction of the cesium, from the direction of both the thin and the thick ends of the wedge. That this was not connected with a certain selective incidence of the cesium on the film is clear from a comparison of curves 1 and 2 (Fig. 4), obtained with the same tube but on different adjacent backings. The difference in the characteristics must be regarded as being conditioned by the structural features of the films for different conditions of crystallization of the condensed film on different backings.

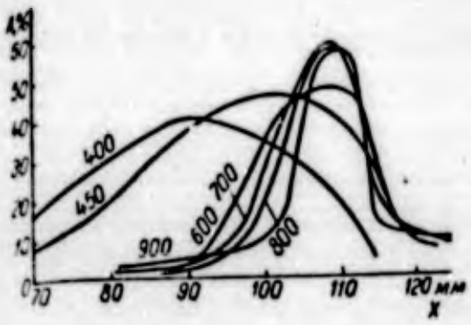

Fig. 3.

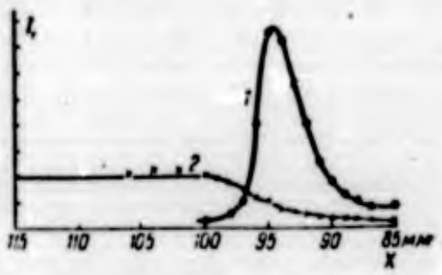

Fig. 4.

Special interest attaches to the results presented in Fig. 5. They relate to a tube, on the inner surface of which a longitudinal strip of thick silver film was first deposited. A silver film of variable thickness, later activated with cesium, was then vaporized both onto the bare glass and the silver strip. Here again curve 1 characterizes the distribution of photocurrent over the film deposited on the bare glass, curve 2 that over the film covering a strip of the same metal. In each case the distribution I(x) can be explained in the light of the data of Figs. 6 and 7. Fig. 6 shows the distribution of the photocurrent over a film on a glass backing for direct illumination $I_1(x)$ (repetition of curve 1, Fig. 5) and for back illumination $I_2(x)$. These curves are compared with the distribution of the coefficients of reflection R(x), transmission D(x), and absorption A(x) over the film. The optical and photoelectric measurements were made at the same time. All the measurements were made with a green light probe. Apart from the distances along the film (x), the abscissa axis shows values of the surface density of the silver, calculated from the law of distribution of the condensate and characterizing the "thickness" of the film.

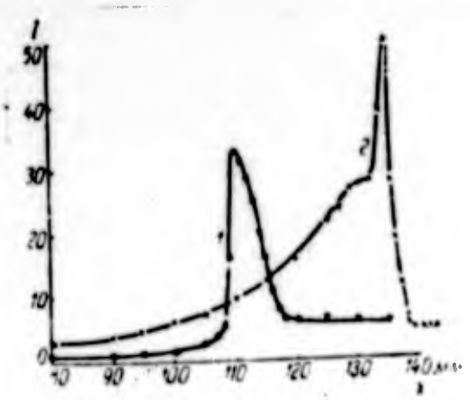

Fig. 5

Working from the thick to the thin end of the wedge, we observe the harmonious variation of the photocurrent from the cathode and the absorption in the silver film

(the presence of adsorbed cesium does not have a significant effect on the optical properties of the film, especially in the area of high optical absorption). However, after reaching a maximum the photocurrents fall sharply, while the values of A vary comparatively slowly. This disturbance in correlation is perfectly natural

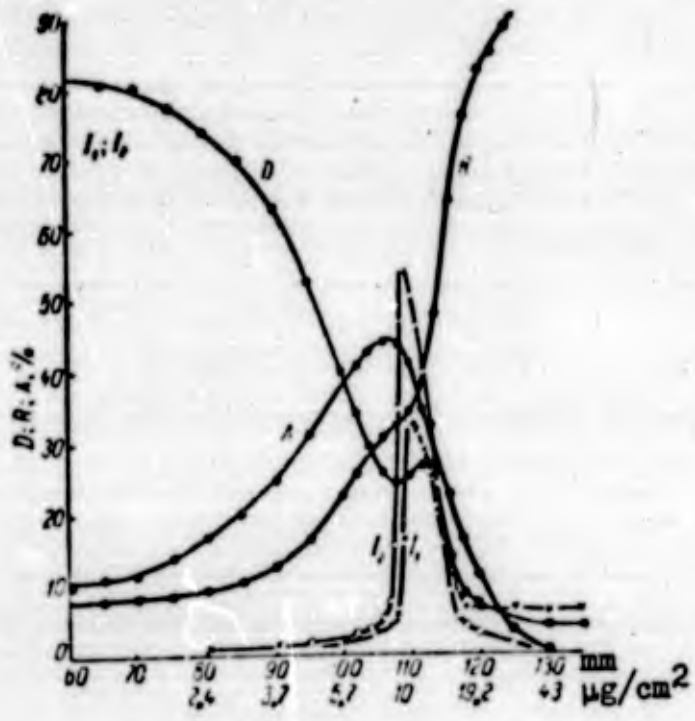

Fig. 6.

according to Morozov and Butslov, whose data show that in this region of thicknesses the conductivity of the film disappears. This fall in the conductivity of a film consisting of isolated particles also conditions the slope of the photocurrent curves in the direction of "thinning" of the film. Thus, we arrive at the conclusion that the enhanced photoelectric emission from a given section of the film is linked with an enhanced optical absorption in the dispersed coating of silver. The correlation in the thinner part is disturbed by the attendant circumstances. If the photo effect is determined by the absorption of light by the particles of silver forming the network of the film, it follows that the really fundamental source of photoelectrons in the photocurrent we measured is not the adsorbed film of cesium, which does not have a significant effect on the optical conditions, but the silver particles themselves.

The right-hand branches of the photosensitivity distribution curves, which rise to a maximum, correspond to states of the film in which the dispersed particles composing it are still not completely isolated and a certain contact is retained between them or a considerable portion of them. This also corresponds to the cases of distribution of silver particles in Ag-O-Cs cathodes, obtained from starting films of Ag_2O, since the conduction of these cathode films is metallic [9]. It might be useful to observe the distribution of the intensity of the photo effect on films treated with cesium as a function of their thickness in investigating the problem of the rational choice of the "thicknesses" of silver films for photosensitive mosaics, where we are interested both in good sensitivity and the best possible isolation of the individual grains making up the mosaic. If the grains formed are too fine (thin end of wedge), the film may lose sensitivity, whereas if the grains are too coarse, it may become conducting.

Having established that the intensity of the photo effect is linked with optical absorption in the under-film, we can now take the intensity of the photo effect from a given cesium-treated metal film as a measure of the absorption of light in the film. This also makes understandable the nature of the distribution of the photocurrent over the silver strip represented by curve 2 in Fig. 5. This curve is reproduced in Fig. 7, together with the distribution curve of the mirror-reflection coefficient R(x). At one end the thick strip of silver was dull. The surface roughness gradually decreased in the direction of the other end, where the strip had a mirror surface. This is depicted schematically at the top of Fig. 7. The regular reflection coefficient R(x) varies in exactly the same way. When a light probe moves off the dull end of the strip, it falls on the mirror of the vaporized film of variable thickness (thick even at this point), deposited on a smooth glass backing, and the value of R suddenly increases. As the roughness of the film increases, so does the photocurrent. Where the dull surface of the film ends, the photocurrent also falls. Hence we conclude that a dull surface absorbs a considerable amount of light. Obviously, the preliminary loosening of a silver surface in order to make the Ag-O-Cs cathode deposited on it more sensitive is intended not so much to increase the effective surface area, as to create the best possible surface for absorbing light.

Note also the following. Ordinarily, in the region of optimal sensitivity of an Ag-Cs film of variable thickness, the photocurrent for back illumination I_2 exceeds that for direct illumination I_1 by about one-and-a-half times. The amounts of light absorbed by the film in the two directions are found to be roughly in the same proportion. The fact that $\frac{I_2}{I_1} \approx \frac{A'_2}{A'_1}$ also confirms the bulk nature of the photo effect of light-absorbing particles of silver. It also shows that the thickness of the silver grains at a given point is equal to or less than the threshold depth for the escape of photoelectrons. If this were not so, we would always have the inequality $\frac{I_2}{I_1} < \frac{A'_2}{A'_1}$, and this would be the greater the more the thickness of the grains exceeded the threshold depth. We can only make a rough estimate of the thickness of the grains. Optimum photoelectric sensitivity corresponds (cf. Fig. 6) to a surface density of the silver in the film of approximately 10 $\mu g/cm^2$. If the film were continuous, its thickness at this point would be $d \approx 10$ mμ. If we assume that the grains of the film cover half the area of the backing, the thickness $d \approx 20$ mμ. Thus, the threshold depth for the escape of photoelectrons from the grains of silver can be roughly estimated at $t > 10$-20 mμ. This result can not be transferred to the massive metal, since the conditions of loss of energy by photoelectrons moving inside the metal will be different for the two cases -- the continuous energy spectrum of the electrons of the conduction band of the massive metal begins to degenerate into a discrete spectrum for fine deposits.

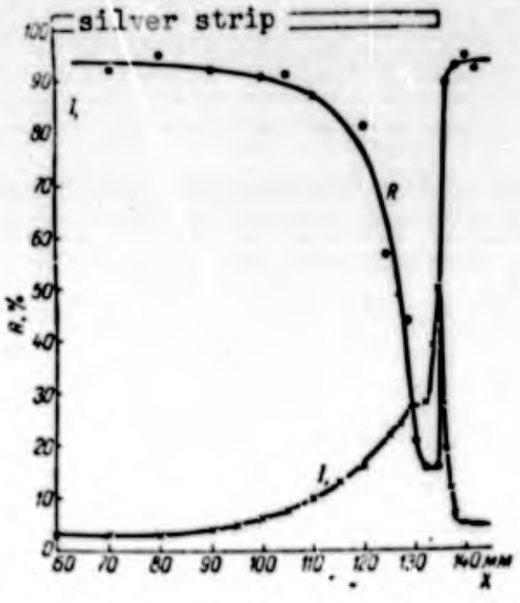

Fig. 7.

The following question arises concerning the intensity of the photo effect

observed with films of the Ag-Cs type. In Fig. 8 we have compared the spectral characteristics of the photo effect, measured under the same conditions and shown to the same scale, for the point of optimum sensitivity of a cesium-treated silver film (curve 1) and for three Ag-O-Cs photocathodes. Curve 2 is for the industrial photocell TsV-4, and curves 3 and 4 for thin-film cathodes of a technical type with sensitivities of 30 and 37 μa/lm. From this comparison it is clear that a film of the Ag-Cs type can in no way serve as a model for an Ag-O-Cs cathode. On the other hand, in the shortwave region of the visible part of the spectrum, the intensity of the photo effect of our film is of the same order as that of the Ag-O-Cs cathodes. This gives us reason to suppose that in the Ag-O-Cs photocathode the separate particles of silver play an important part in the photoelectric emission, at least within a certain region of the spectrum.

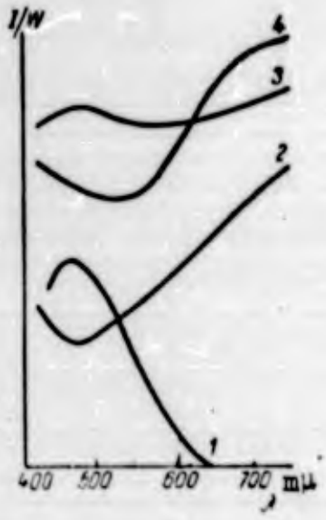

Fig. 8.

Note that in the experiments described dark conduction through the glass did not interfere with the measurements. This was probably because the energy of adsorption of the cesium atoms was greater on the silver films than on the glass. As further cesium is admitted to the tube, the ad-film becomes thicker than the optimal, the photosensitivity of the optimal section of the film falls, and finally conduction through the glass of the tube appears. Moreover, if too much cesium is admitted to the tube, the optical properties of the silver film change. Visually, what happens is that the band of higher transmission in a film of variable thickness becomes less well expressed and vanishes, and the previous coloring of the thin edge of the silver film gets fainter and disappears.

The Photo Effect of Mosaic Films of Silver Coated with Complex Films of Oxygen and Cesium

The system investigated was further complicated by replacing the adsorbed film of cesium with an ad-film of a more complex type -- Cs-O-Cs. The experiments were conducted with tubes fitted with two branches. One of the branches, connected across a narrow inlet, contained an ampoule of cesium, which was broken electromagnetically, the other an ampoule of oxygen. After the silver film had been deposited, the cesium ampoule was broken and the tube sealed off from the pump. After a more or less optimal ad-film of cesium had been formed, the oxygen ampoule was broken, whereupon the photocurrent immediately fell to zero, which indicated the total oxidation of the cesium ad-film. The excess oxygen was absorbed with a drop of cesium in the first branch. Further admission of cesium vapor into the tube led to the adsorption of cesium atoms on the Cs-O ad-film. The dynamics of the formation of the complex film may be observed in the distribution of the photocurrent. Certain results of such observations are shown in Fig. 9. Here a decrease in the values of x corresponds to a decrease in the thickness of the silver film. The coordinate x = 120 mm corresponds roughly to the end of the thick part of the film, which terminates here in a steep wedge of penumbral origin from the edge of the screen, where the whole range of structural features of the film is repeated within a short section.

Curve 1 was obtained at a certain moment after the adsorption of the cesium onto the Ag-Cs-O. The nature of the distribution of the photosensitivity over the film is the same as in the preceding cases. After a certain time the measurements

gave curve 2. For checking purposes, we measured the distribution of photosensitivity in the region of the steep wedge at the opposite end of the film, closer to the branch containing the cesium. Generally speaking, the nature of the distribution and the optimal sensitivity were the same as for the long wedge. This once again indicates that the sensitivity distribution is determined by the structure of the silver film. Curves 3 and 4 were obtained after successive intervals of time. They show how the region of high sensitivity gradually shifts ever further towards the thin part of the wedge. This is due to the gradual broadening - as more cesium is admitted -- of the zone of sufficient conductivity of the film. At the same time there is a fall in sensitivity in the region of the previous maxima, which indicates the gradual thickening of the film of cesium in this region and its passage beyond

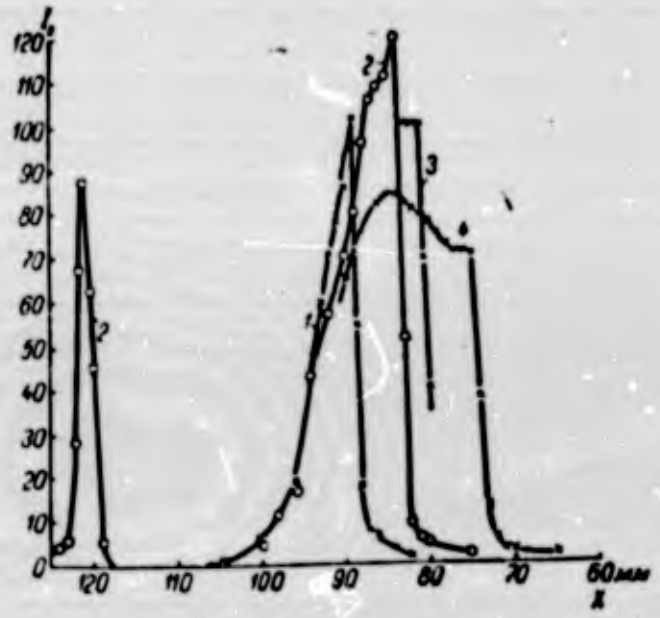

Fig. 9.

the optimum. Fig. 10 shows how this transition from a Cs ad-film to a Cs-O-Cs ad-film affects the photosensitivity of the optimum part of the cathode. Curve 1 represents the spectral characteristic of the photocurrent $I_2(\lambda)$ (not referred to equal energies) for Ag-Cs. Curve 3 represents the same thing for Ag-Cs-O-Cs. Curves 2 and 4 are, respectively, the spectral characteristics referred to equal incident light energies $I_2/W = f(\lambda)$.

Actually, we do not really know how the complex oxygen-cesium film formed in the experiments described is really composed, and the designation Cs-O-Cs is purely provisional, representing more the sequence of the operations than the actual physical picture. If we were to deposit a great deal of cesium and oxygen on the surface, i.e., created a thick film of Cs and O_2, we might confidently talk in terms of an oxygen-cesium compound (exactly which is another question), for example Cs_2O. From the physical standpoint, this means that we would speak of a film with the crystal lattice of cesium oxide. What is represented by the case, intermediate between Cs and Cs_2O, of an adsorbed film is an interesting and complex problem requiring special investigation. We can only say that the film obtained on the particles of silver, provisionally called Cs-O-Cs, has a greater dipole moment than a Cs film, and shifts the boundary of the photo effect further into the red region of the spectrum.

As we shall see below, the Cs-O-Cs-O-Cs film is also a type of complex film, intermediate between Cs and Cs_2O-Cs. Accordingly, for this too we shall retain the clumsy form of designation proposed above.

In carrying out several alternating cycles of treatment with oxygen and cesium, we used the same experimental tubes with only one modification. This consisted in fitting them with a set of tubes with thin-walled glass diaphragms designed to separate the space of the tube from the external space. These diaphragms could be broken electromagnetically under a vacuum. This made it possible to unseal the tube at a certain stage in the formation of the cathode and after inspection reseal it to the vacuum apparatus, and carry out further operations. In such cases the films were oxidized on the vacuum apparatus itself.

The nature of the distribution of the photocurrent over the film remained the same as in the previous cases. Only when a comparatively thick oxygen-cesium film was formed, did the region of sensitivity of the cathode also extend to the thinnest part of the wedge. In this case the intervals between the silver grains were clearly bridged by the cesium oxide film.

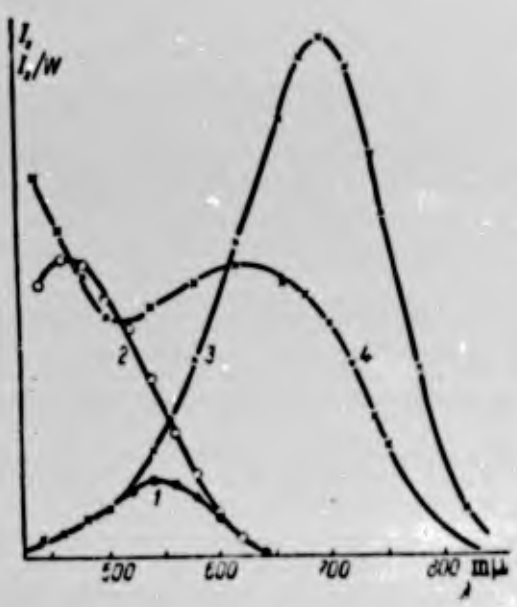

Fig. 10.

By oxidizing a film of the Cs-O-Cs type and then again activating it with cesium, we obtained a further change in the spectral characteristic of the photo effect and the integral sensitivity of the cathode in the region of high sensitivity. This is illustrated by the data of Fig. 11. Curve 1 represents, to another scale, curve 3 of Fig. 10; curve 2 characterizes a cathode in the Ag-Cs-O-Cs-O-Cs stage. For the sake of comparison, the broken-line curves 3 and 4 represent, to the same scale, data relating respectively to one of the thin-film cathodes of the technical type, mentioned above, and to the cathode of the TsV-4 photocell. It is clear from the figure that the shortwave branch of the characteristic of the film in question is not inferior in height to those of the technical cathodes, but its longwave branch falls much more steeply than those of the latter. It follows that even the Ag-Cs-O-Cs-O-Cs model still does not give the characteristic of an ordinary Ag-O-Cs photocathode.

The Photo Effect of Cathodes of the Ag-Cs_2O-Cs Type

If the oxygen-cesium film continues to grow, we get further displacement of the spectral characteristic of the photo effect into the infrared region, but at the same time its maximum is reduced. In general, however, we still get a cathode with a characteristic of the spectral sensitivity similar to that of ordinary cathodes. The changes in the spectral characteristic are illustrated in Fig. 12. Here curve 1, like curve 2 in Fig. 11, relates to a cathode of the Ag-Cs-O-Cs-O-Cs type. Curve 2 was obtained after the subsequent growth of an oxide film. We shall provisionally label this cathode Ag-Cs_2O-Cs. After this cathode had been activated by depositing additional silver on its surface, we obtained curve 3. Curves 4 and 5 relate to the above-mentioned technical photocathodes. Fig. 13 shows the same curves 1, 2, 3, referred to equal incident light energies.

From the characteristics of the cathode of the Ag-Cs-O-Cs-O-Cs type we see that in the region 700-750 mμ it possesses the same sensitivity as an ordinary Ag-O-Cs photocathode, though its characteristic falls comparatively sharply in the red direction. Such cathodes might be useful in certain special cases, where the red sensitivity of an Ag-Cs cathode is already low and the sensitivity of an Ag-O-Cs cathode in the infrared is for some reason undesirable.

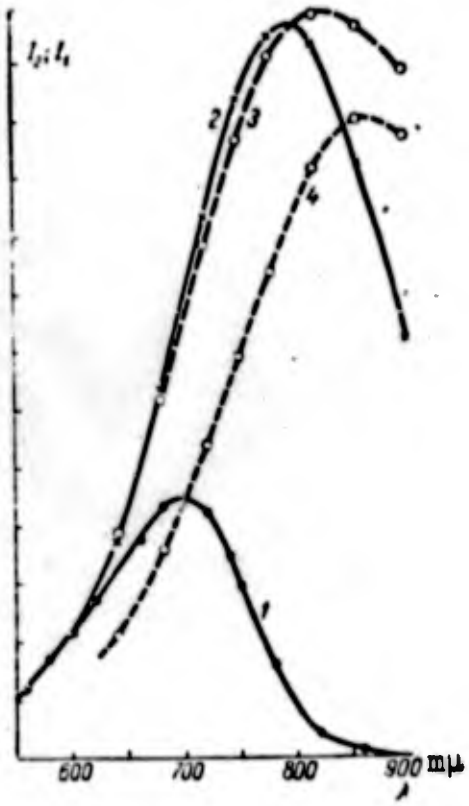

Fig. 11.

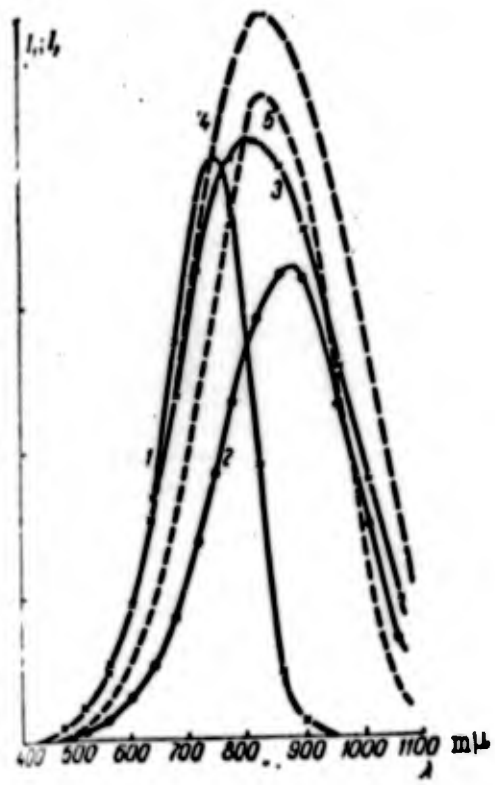

Fig. 12

From an examination of curves 2 and 3 we see that by artificial means it is possible to obtain cathodes similar to ordinary Ag-O-Cs cathodes in integral and spectral sensitivity. This suggests that in both cases we are dealing essentially with one and the same cathode. Accordingly, the conclusions that may be derived from a study of artificially prepared cathodes will also relate to cathodes of the technical type prepared by ordinary means. The advantage of artificial cathodes for investigation purposes resides in the possibility of a more detailed experimental analysis of the parts played by certain factors. Moreover, this method of preparing cathodes can also be used to obtain mosaics.

On comparing curves 1 and 2 we see that as the cesium oxide film thickens, the very sharply expressed spectral maximum falls, and the curve of spectral sensitivity is displaced further into the infrared; however, this is not accompanied by the same tendency to a change in the optical properties of the cathode. On the contrary, the accumulation of a thick film of cesium oxide on a dispersed film of silver leads, as the measurements show, to a relative increase in absorption in the shortwave region. The characteristic of the infrared component obtained by subtracting curve 1 from curve 2 is given by the solid curve 4. If we bear in mind that in state 2 the sensitivity present in state 1 is suppressed, then, actually, we should subtract

from curve 1 values less than the ordinates of 2, the more so the further to the left the values we take. There the true characteristic must have the form represented by the broken curve 4. If this were related not to wavelengths, but to frequencies, we would also obtain a characteristic approximating the bell-shaped type, similar to that obtained, for example, for the absorption of the coloring centers of alkali-haloid salts. It is possible that our curve characterizes the probability of photoionization of the cesium ad-atoms or the excitation of electrons from certain local levels in the cesium oxide lattice. In any event, this increase in the infrared sensitivity is not linked with the previous emission centers but connected with the appearance of new centers, the spectral characteristic of the photo effect of which is given by curve 4, while, as follows from the above, their part in the total absorption of light by the cathode is inconsiderable.

It is typical that these centers never appear in the presence of thin oxide films of the type Cs-O-Cs and Cs-O-Cs-O-Cs, but come into action only when the film continues to grow, although nothing new, apart from the same oxygen and cesium, has been introduced into the cathode. From this it follows that the appearance of the new centers is linked with the structural conditions in the oxygen-cesium film itself. It must be assumed that this is connected with the formation of the cesium oxide lattice, when we have to deal not with a film of the complex type on the cathode surface but with a film of a definite substance with its own crystal structure. This is bound up both with a transition to new surface conditions, including new adsorption conditions (this manifests itself in a further shift in the red boundary of the photo effect), and with the possible appearance of local electron levels in the lattice, which previously simply did not exist.

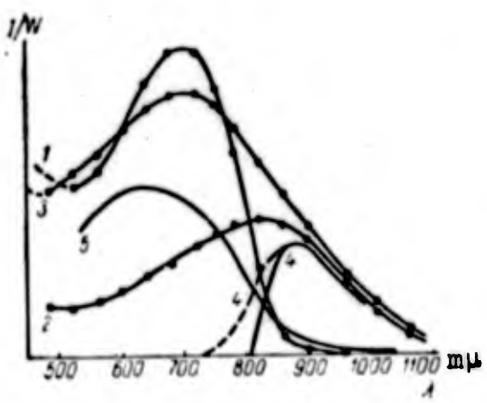

Fig. 13.

After the deposition of the silver we went from curve 2 to curve 3, which indicates the restoration of emission to the former maximum and virtually no change in infrared sensitivity. In conjunction with the previous result, this leads us to the important conclusion that the fundamental sensitivity of a cathode in the region of the spectral maximum is essentially determined by the photo effect of the silver particles in the surface layer of the cathode. When these particles are plastered over with a fairly thick layer of oxide, the sensitivity falls in the region of the principal maximum. A second deposition of silver in the surface layer of the cathode restores the suppressed sensitivity in this region. It should be noted that a number of authors [3, 8, 9], particularly Yumatov, have observed a displacement of the maximum of the spectral characteristic of the photo effect of ordinary Ag-O-Cs cathodes toward the shortwave side of the spectrum following the deposition of silver. Generally speaking, in this case, the cathodes are characterized by a maximum spectral sensitivity lying more on the shortwave side (700-750 mμ), a finding which also agrees with our own data, as compared with the values ordinarily accepted for Ag-O-Cs cathodes without a silver deposit (800-850 mμ). Finally, it is known that no one has succeeded in preparing a silverless oxygen-cesium cathode with a sensitivity of the same order as that of an Ag-O-Cs cathode.

How can we picture what happens on the surface of a cathode after it has been treated with additional silver? Let us recall the effect observed on a glass surface. When a silver film is deposited on glass between two contacts, at a certain

stage these contacts are closed. If no more silver is deposited, at room temperature the conductivity of the film will begin to decrease and, finally, disappears. It is well known why this happens. The film is dispersed. The atoms that form it are gathered into microcrystallites and expose a considerable portion of the surface of the glass. When we deposit silver on a cathode, we cover its surface with a silver film, which leads to a fall in sensitivity. When deposition ceases, the sensitivity of the cathode at room temperature is slowly restored. It is difficult to believe that at room temperature the film could escape so quickly from the surface by the diffusion of the silver into the bulk of the cesium oxide. It is more natural to assume that the film on cesium oxide behaves in the same way as a film on glass -- the silver is gathered into microcrystallites, laying bare a corresponding area of the cathode. The sensitivity of such a cathode increases on heating. At higher temperatures the diffusion and migration processes and, perhaps, displacement processes of a more macroscopic character connected with the continuing crystallization of the silver are activated, and the grains of silver become covered with a complex film. If cesium atoms are present in the cathode in the free form, they may migrate to the surface of the grains of silver even at room temperature.

Now, let us consider the curve obtained by subtracting curve 3 from curve 2. This is represented by curve 5, which is the spectral characteristic of the photo effect of the added particles of silver. If these particles were covered with a film of cesium ad-atoms, the characteristic would have a form similar to curve 1 (cf. Fig. 8). In fact, we obtain a characteristic intermediate in form between curves 4 (Fig. 10) and 1 (Fig. 13), characterizing the photo effect of particles of silver coated with a complex film.

From the above it follows that the ideas about Ag-O-Cs cathodes, according to which the colloidal particles of silver are a neutral impurity as far as the photo effect is concerned, are incorrect. The results obtained confirm the main thesis of Lukirskiy and Khurgin, to the effect that, in regard to the mechanism of the Ag-O-Cs cathode, we must above all bear in mind the photo effect of the colloidal silver particles. In fact, the latter play an important part in the photoelectric emission of Ag-O-Cs cathodes, and when they are not covered with a thick layer of cesium oxide they are the chief source of photoelectrons in the region of the spectral maximum of the photo effect. The part of the Lukirskiy-Khurgin hypothesis that assumes the high transparency of the cesium oxide for photoelectrons from the silver and attributes to the silver particles the entire spectral characteristic of the photo effect of the Ag-O-Cs cathode is not confirmed. A thick layer of oxide considerably reduces the photoelectric emission of the silver particles. It is possible that an important part in this is played by the transparency for electrons of the silver-cesium oxide interface, from the moment when the lattice of the latter is formed. The photo effect in the infrared region is connected with other emission centers, probably cesium ad-atoms, with which most authors link the whole of the main part of the spectral characteristic and with which we link the characteristic of curve 4 (Fig. 13). In the ultraviolet region the photo effect of the cesium oxide is probably dominant.

There can be no doubt that in the Ag-O-Cs cathode we are dealing with several types of photoelectron sources, each of which has its own spectral characteristic, and with at least two principal structural elements (particles of Ag and Cs_2O), each of which has its own optical absorption characteristic. The superimposition of all these factors complicates the problem of comparing the optical and photoelectric properties of the finished cathode, and the results of such a comparison of the over-all characteristics remain obscure.

Bibliography

1. Lukirskiy, P. I. & Khurgin, Ya. L. Sow. Phys., 7, 106-107, 1935.
2. Sayama, Y. JOSA, 39, 162, 1949.
3. Yumatov, K. A. ZhTF (J. Theor. Phys.), 22, 177, 1952.
4. Borzyak, P. G. & Morgulis, N. D. DAN SSSR (Proceedings of the AS USSR), 61, 625, 1948; Borzyak, P. G. ZhTF, 20, 934, 1950.
5. Vekshinskiy, S. A. Novyy metod metallograficheskogo issledovaniya splavov (A New Method of Metallographic Investigation of Alloys), Gostekhizdat, M.-L., p. 23, 1944.
6. Morozov, P. M. & Butslov, M. M. ZhTF, 16, 857, 1946.
7. Sennett, R. S. & Scott, G. D. JOSA, 40, 203, 1950.
8. Khlebnikov, N. S. & Sinitsyn, P. A. ZhTf, 10, 1919, 1940.
9. Asao, S. Proc. Phys.-Math. Soc, Jap., 22, 448, 1940.

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