PHOTOELECTRIC PROPERTIES OF THIN UNBACKED GOLD FILMS

By Ralph P. Winch
Department of Physics, University of Wisconsin

(Received May 25, 1931)

Abstract

Unbacked films of gold 2×10^{-6} cm thick were produced and studied to determine their photoelectric behavior. These films did not hold a constant photo-emission, but showed a rapid increase in emission with exposure to ultraviolet light. The increase in photo-current was 136 fold and was accompanied by a shift in long wave limit of 576A. Solid gold and silver were given similar treatment and showed a like effect. This increase is explained on the basis of outgassing caused by ejected electrons removing gas from the surface. The final long wave limit reached by the gold films is compared with that for the mass metal when outgassed by severe heat treatment.

THIS work was undertaken with the view of comparing the characteristics of free films with the results of previous workers[1] who used films of metal backed with quartz. Their results showed interesting differences between the photo-emission from the incident and emergent sides of a metal film. The effect of the backing was uncertain so it seemed worth while to attempt the same study using unbacked films.

Unfortunately the thinnest films which it was found possible to remove from their backing were 2×10^{-6} cm thick. Compton and Ross[1] found, for backed films of gold, that films thinner than 8×10^{-7} cm were imperfectly conducting due to isolated regions not in conducting contact with the rest of the film. Since the unbacked films must be sufficiently homogeneous to support themselves, and for photoelectric studies must be large enough so that the image of the source may be focused entirely on them, it is not surprising that they must be considerably thicker than the limit set by Compton and Ross.

The films were produced by a method suggested by Laub and Ruppert.[2] The method was, in brief, to sputter the metal on the surface of a polished rock salt crystal and dissolve the rock salt in water leaving the film free. This film was then caught on a copper ring which gave it rigidity for handling and mounting. The films for which data is given here were approximately 2×10^{-6} cm thick. The thickness was measured by light absorption[3] using data obtained by Meier[4] and Hagen and Rubens.[5]

[1] Compton and Ross, Phys. Rev. **13,** 374–391 (1919); Stuhlman, Phys. Rev. **13,** 109 (1919); **2,** 199 (1913); **4,** 195 (1914). Robinson, Phil. Mag. **32,** 421–425 (1916); **25,** 115–132 (1913).

[2] Laub and Ruppert, Phys. Zeits. **27,** 452.

[3] Wood, "Physical Optics," p. 465.

[4] Meier, Ann. d. Physik **31,** 1017 (1919).

[5] Hagen and Rubens, Deutsch Phys. Ges. **4,** 5 55–63 (1902).

The vacuum apparatus and electrometer were the same as used for the study of the photoelectric properties of silver.[6] Pressures of 10^{-7} mm of Hg or less were maintained throughout the experiment. The long wave length limit tests were made by placing absorption cells in the path of the incident light and immediately photographing the spectrum of the transmitted light using a quartz spectrograph. Solutions of various concentrations of tartaric acid in distilled water were found to cut off quite sharply in the desired region of the spectrum. In this way the longest effective wave-length could be found.

Photoelectric Outgassing

The photo-emission from these gold films did not remain constant but increased very rapidly on exposure to ultraviolet. This effect was noted first by Millikan[7] while studying silver, zinc, iron, nickel, and copper in the solid form.

With prolonged exposure of the film to ultraviolet under conditions for photo-emission the long wave limit shifted from about 2000A to 2482A. Long continued exposure failed to make 2537A effective and the emission remained constant during this time.

With an identical film under conditions as nearly identical as could be determined the field about the film was reversed so that emitted electrons travelled against the field until their kinetic energy was lost and then returned to the film. This time the long wave limit shifted on exposure to ultraviolet, more rapidly than before and, although it started at the same place, it ended near 2576A. While in the former case 2482A was the longest wave-length to become effective with continued exposure, in this case 2537A became effective in 64 hours and, when equilibrium was reached after 250 hours of exposure, 2576A was the longest effective line. One hundred hours additional exposure did not change either the long wave limit or the emission. During this latter change of long wave limit the photo-current increased 136 fold.

Photographs, with a quartz spectrograph, showed that the films were transmitting light down to a wave-length of 2259A but that only approximately 10 percent of the energy in the lines below 2537A was being transmitted.

While the incident face of the film was being exposed as discussed above the opposite face was affected only by the transmitted light. It showed an increase in emission proportional to the ultraviolet transmitted by the film but no such increase as shown by the incident face. The second face was now exposed for 32 hours through a filter which absorbed all wave lengths below 2800A but which transmitted 55 percent of the total energy of the arc as measured with a thermopile. During this time there was no change in the emission. At the end of the 32 hours the filter was removed and the emission immediately began to increase changing by 5.6 fold in the next 32 hours. Continued exposure of this face showed a very close repetition of the change discussed for the former face.

[6] Winch, Phys. Rev. **37**, 1269–1275 (1931).

[7] Millikan, Phys. Rev. **30**, 287–288 (1910); **29**, 85 (1909); **34**, 68–70 (1912).

A repetition of this experiment using a disk of solid gold showed an increase in photo-emission, and shift of long wave limit from 2000A to 2482A which took place much more slowly than with the thin films.

After 360 hours exposure of the film and 160 hours exposure of the solid gold the light from the arcs was cut off and frequent readings taken to determine the change of emission on standing without exposure to ultraviolet. The film was found to hold a constant emission for about 3 hours, and then gradually decrease. The solid gold held constant for about 1.5 hours and then gradually decreased. This shows that the equilibrium gas conditions change very slowly. Similar curves taken earlier in the process showed a more rapid falling off of emission on standing unexposed.

A filament of silver, 0.025 mm thick and 3 mm wide, was given treatment similar to that given the gold films and solid gold in order to determine whether this effect of ultraviolet light is unique with gold. The increase in emission was analogous and was accompanied by a shift in long wave limit. There was one marked difference between the silver and gold. For gold there was a rather abrupt increase in photo-current each time the shift in long wave limit took in a new line of the mercury arc followed by nearly constant emission until the next line was reached. However in the case of silver the emission increased continuously whether a new line became effective or not. As an example of this, after seven hours of exposure of the silver to ultraviolet, 2482A was the last effective line; and careful tests made after 15 hours showed that it was still the last effective line, but the emission had doubled during this time. The long wave limit is undoubtedly shifting continuously and for silver the "quantum efficiency" apparently shifts continuously as well. The change of the silver specimen was never carried as far as it would go.

Conclusions

This increase in emission and shift of long wave limit is analogous to that observed when metals are given heat treatment for outgassing.[6] The evidence given here points to the theory that electrons ejected photoelectrically remove gas molecules from the surface of the metal. Heating due to absorbed radiation, could not explain the results since the two faces of so thin a film would be at nearly the same temperature and hence would increase in emission together. This was not the case. Also the increase in temperature of the mass metals, under the conditions used for this study, would be very small. The fact that the exposure of the film, through the filter which cut out all light effective for photo-emission, did not produce an increase points to the fact that photo-emission is the cause of the outgassing. If ejected electrons remove gas from the surface it is conceivable that returning electrons should do the same. The part of the experiment where the field was reversed showed this to be the case.

Morris[8] showed that the long wave limit of thoroughly outgassed gold at room temperature is near 2560A. The final value arrived at for gold films

[8] Morris, Phys. Rev. **37**, 1263–1268 (1931).

after long continued exposure was near 2576A. The long wave limit is a rather indeterminate quantity since the curves for emission per unit light intensity against wave-length show an exponential tail along the wave-length axis. Consequently these two values for long wave limit at room temperature are in good agreement, rather better agreement than one would expect from the history of the specimens previous to their determination. It will be noted in Morris' work that the emission for gold increased very rapidly to a high maximum with heating and then decreased finally settling down to a steady value. At the same time the long wave limit shifted first to above 3000A and then back to the stable value of 2560A. This is quite in contrast with the behavior of the thin films where the emission increased and the long wave limit shifted in one direction continuously with exposure to ultraviolet ultimately settling down at the final value. Since the film is so thin that light passes entirely through it and the exposure was long continued on both surfaces it is not inconceivable that the film is in the same stable condition reached by the solid gold subjected to severe heat treatment. On the other hand it is also possible that the final condition of the film corresponds to an early stage in the outgassing process when the long wave limit is on its way toward 3000A. In this case one would have to conclude that the film was not outgassed. The first great increase in sensitivity of the solid gold specimen is probably due to the particular combination of gas (coming from the interior or on the surface) and metal existant at that time and is not characteristic of the metal. This high maximum has been shown by other metals given similar heat treatment.[6] It is possible that with the thin film the combination for the high maximum never existed but that the final condition was the same as with the solid gold.

Dillon[9] of this laboratory has used this method of outgassing on a single crystal of zinc which was made in vacuum and hence had gas only on the surface. The method is particularly useful for those cases where outgassing by heat treatment cannot be employed. By such treatment a stable condition is reached, but its relationship to the stable condition reached by heat treatment must be more carefully studied.

In conclusion the writer wishes to express his appreciation of the many suggestions and continued help generously given by Professor C. E. Mendenhall, under whose direction this work was carried out.

[9] Dillon, Phys. Rev. August 1, 1931.