

## Photoconductivity of Lead Sulfide Films

G. W. MAHLMAN\*

*Electronics Corporation of America, Cambridge, Massachusetts*

(Received April 16, 1956)

Extensive experimental data have been taken on thin photoconducting films of lead sulfide of the chemically-oxidized type. Conductivity of the films in the temperature range 77°–300°K depends greatly on the amount of oxidation received by the films. Activation energy approaches a maximum value of 0.35 electron volt, but may have any value down to zero depending on the temperature range, amount of oxidation, and the illumination. Time constants as well as conductivity have been measured at different temperatures and illuminations, and in general tend toward a reciprocal relationship though the detailed behavior is more complicated than a simple reciprocity. Other important properties measured include spectral response and transient response to large changes in illumination.

### INTRODUCTION

EXPERIMENTAL results are presented concerning certain important physical properties of thin photoconducting films of lead sulfide. The properties which have been measured are: (1) conductivity as a function of temperature for films in the dark and for films illuminated with various amounts of radiation, (2) the transient response of films (i.e., the rise and decay of conductivity as a function of time after the interruption of radiation) as a function of temperature and illumination, (3) response (photocurrent) at constant temperature as a function of illumination, and (4) spectral response characteristics for many cells at different temperatures.

All of these properties depend on the processing received by the films, particularly on the amount of "oxidation" which they receive. Some properties, such as conductivity, vary tremendously with processing. Since chemically oxidized films are under the best control with respect to processing, and are the most uniform, almost all data have been taken on this kind of films.

The following paper by Slater<sup>1</sup> interprets some of the experimental results presented in this paper.

### EXPERIMENTAL PROCEDURE

#### Preparation of Photoconductive Films

There are at least three methods of preparing photoconductive thin films of lead sulfide. The first method is to evaporate material from a bulk slab of lead sulfide onto the substrate material, usually glass. To render the thin evaporated film photoconducting, the evaporation is done in a low pressure of oxygen. The second method of preparation is by a chemical deposition analogous to a silvering process. Sensitization is accomplished by baking the chemically deposited film at a rather high temperature in the presence of oxygen. The third method is again to deposit chemically the lead sulfide on glass plates, only in this method a chemical oxidizing

agent is present in the chemical baths as the deposition is taking place. This film is sometimes partially sensitive as it comes from the baths but is always baked in vacuum at a relatively low temperature to make it more sensitive.

Almost all of the basic research data have been taken on chemically oxidized films deposited in a single coat on glass substrates. In the first place, much experience with films shows that these films are the most uniform in their response to light. That is, if a small spot of light is moved over the surface of the film between the electrodes, the increase in current through the film due to the spot of light is most nearly constant for films prepared in this way. Uniformity has also been checked by measuring the potential variation with distance from one of the electrodes. Films which do not respond uniformly to a spot of light also show nonlinearity in potential distribution.

Further information concerning the uniformity and surface structure of PbS films can be obtained by taking electron-microscope photographs of the surfaces of the films. Figure 1 shows photographs of shadow-cast collodion replicas of two PbS films. Figure 1(a) is a photograph of an unoxidized chemically deposited film. The crystallites are as large as one-half micron on an edge. When oxidant is added to the baths to make photosensitive films, the crystallites are broken up into smaller ones. The photograph in Fig. 1(b) shows upon close examination, that the crystallites are approximately cubic and about 0.1  $\mu$  or less on an edge. From the electron-microscope studies completed to date, it is known that crystallite size does not vary greatly as the amount of oxidant is varied until this becomes very nearly zero.

A second reason for the choice of chemically oxidized films is that the amount of oxidation received by the films is under the closest control for this method of preparation. The amount of oxidation received by a film determines its physical properties to a very great extent. Unless the film is oxidized in just the right amount, maximum response to radiation will not be obtained. In the work to follow, the relative amount of oxidizing agent present in the chemical baths when the

\* Now at Sylvania Electric Products, Electronics Division, Woburn, Massachusetts.

<sup>1</sup> J. C. Slater, Phys. Rev. **103**, 1631 (1956), following paper.

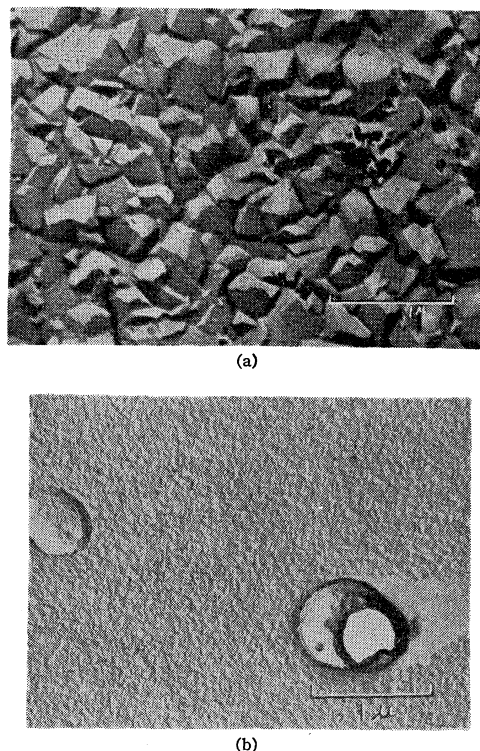


FIG. 1. Electron microscope photographs of lead sulfide films. (a) Chemically deposited film; (b) chemically oxidized film.

film was made will be given as the "percent oxidant." Presumably the greater this percentage, the more oxidized the film is, although no direct methods have been devised for determining just how much oxygen is in the film or in what form the oxygen exists.

### Experimental Apparatus

In order to protect the PbS films from changes due to moisture and other substances in the air, the films are enclosed in a high-vacuum cell. Figure 2 is a diagram of such a cell. Gold electrodes are evaporated onto the PbS film surface and electrical contact made via Inconel springs welded to tungsten leads. A thin-walled bubble window transmits 50% or more of incident radiation to wavelengths greater than  $4\ \mu$ . The ball of aluminum foil shown was found to be effective in keeping heat away from the PbS film during the process of constricting and sealing off the end of the cell. The films are baked on the vacuum system for two hours and then sealed off at pressures of about  $10^{-6}$  mm Hg or better.

Most of the physical properties of PbS films are measured by the apparatus shown in Fig. 3. The PbS cell is placed within an apparatus (designed by R. H. McFee), shown in detail in Fig. 4, which permits the temperature of a copper container surrounding the cell to be varied between  $77^\circ$  and  $400^\circ\text{K}$ . The operation of this apparatus is evident from the figure—by sending

the proper amount of heater current through the heater surrounding the inner copper cylinder, the temperature of this cylinder can be maintained at a higher value than that of the outer copper cylinder. Temperature can be maintained within one degree at any value within this  $77^\circ$ – $400^\circ\text{K}$  range for any desired length of time; this is accomplished by an on-off heater-current control operated photoelectrically from a galvanometer which measures the thermocouple potential of the inner copper container.

In series with the PbS cell are a bias battery and a load resistor  $R_L$ . Some PbS cells when cooled have resistances exceeding  $10^{13}$  ohms. These high values of resistance can be readily measured by the use of a dc electrometer voltmeter by employing load resistances up to  $10^{11}$  ohms. Bias voltage need not be very high for these measurements— $22\frac{1}{2}$  v have been used for almost all the measurements.

Various sources of radiation have been employed. Tungsten lamps are the most convenient source of radiation, and they operate at such a high temperature that over 90% of the radiation from them lies at wavelengths shorter than the cutoff of the PbS films (i.e., below  $2.6\ \mu$ ). The radiation from tungsten lamps may be calibrated by comparison with that from a blackbody at known temperature. In this way one knows the irradiance ( $\text{w}/\text{cm}^2$  of radiation of all wavelengths incident on the PbS film) as a function of the distance of the lamp from the film.

For measurements of spectral characteristics, a Beckman model IR-2 infrared spectrophotometer has been converted for use as a monochromator. This instrument may be used to illuminate the films in a narrow band of wavelengths in the wavelength region from 1 to  $15\ \mu$ . The radiation is chopped at 10 cps and amplified in the instrument by a tuned amplifier having a very low noise level.

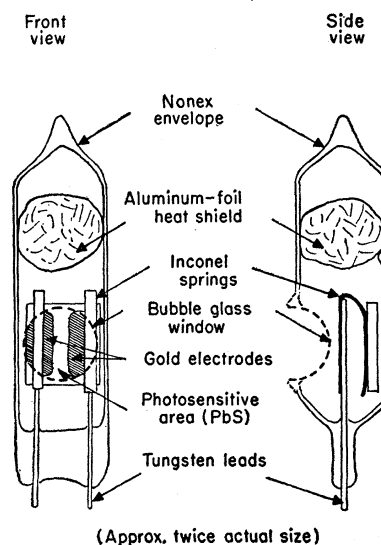


FIG. 2. Diagram of a PbS film research vacuum cell.

For studies of the transient response of PbS cells, radiation from a tungsten lamp is chopped in a square-wave fashion by a mechanical chopper, designed specifically for this work. The time constants of PbS cells vary from a few microseconds to several tenths of a second and therefore a considerable range of chopping speeds must be covered by the equipment. For certain measurements background light from another tungsten lamp is superposed on the modulated light. Since the unmodulated light may be very intense compared to the modulated, mechanical vibration of the chopper must be kept at a minimum in order to minimize unwanted mechanical modulation of the background radiation.

For the measurements of transient response of PbS cells, voltage amplifiers with a frequency range from 0 cps to 100 kc/sec were required. Ordinary ac coupled amplifiers are adequate when time constants are not too long and when cell resistance is not too high. However, when PbS films are operated at low temperatures, cell resistance may exceed  $10^{13}$  ohms and time constants may become very long. In order not to lose too great a fraction of the usable signal response, the load resistance  $R_L$  should approach the PbS cell resistance in value. However, the product of  $R_L$  and the effective input capacity  $C_i$  of the amplifier must be substantially less than the time constant  $\tau$  of the PbS being measured, i.e.,  $R_L C_i \ll \tau$ . To satisfy this condition we must use special feedback amplifiers having very low effective  $C_i$ . However, the irreducible minimum for  $C_i$  is the parallel combination of the capacity across  $R_L$  and that across

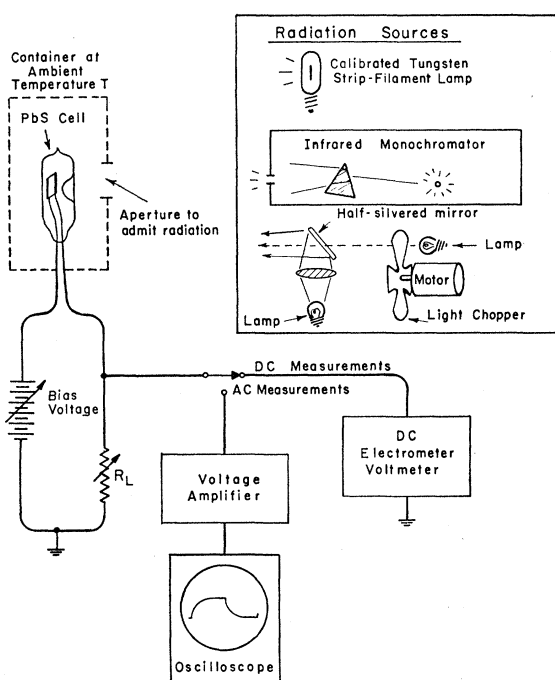


FIG. 3. Diagram of experimental apparatus.

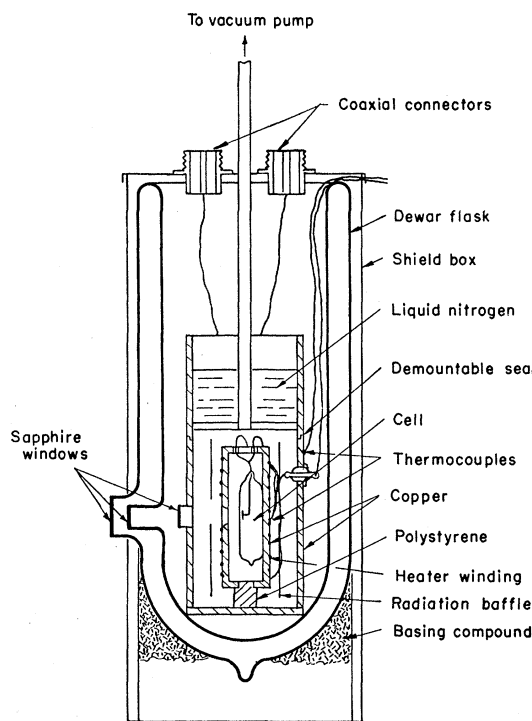


FIG. 4. Cell cooling system.

the PbS cell; this has been measured as 1 or 2  $\mu\text{f}$ . The amplifier shown in Fig. 5 is direct-coupled in order to measure long time constants. The first stage is operated electrometer-tube fashion to keep down grid current, and 100% feedback is employed (voltage gain  $\approx 1$ ) to keep  $C_i$  very small. The input circuit (not shown in the figure) has a bias battery, PbS cell, and load resistor in series, the latter being connected between the grid of the first stage and the feedback loop.

For some of the transient-response measurements, a null-match type of measurement was done. In this type of measurement, a square-wave reference voltage is generated which is in phase with the square-wave light incident on the PbS film. This voltage is applied across an RC integrator circuit with known values for  $R$  and  $C$ . The output is an exponentially rising and decaying voltage having a known time constant  $\tau = RC$ . Output voltage is continuously variable. This voltage is mixed  $180^\circ$  out of phase with the PbS-cell signal. In most cases one finds that the mixed signals will cancel if the amplitude of the signals is adjusted to be equal. This means that the PbS current rises and decays in an exponential way quite accurately under most conditions, and may be described by the time constant  $\tau = RC$ .

The thickness of chemically oxidized films may be determined with an accuracy of about 20% from the difference in weight of the substrate before and after deposition of the film. Density of the film is assumed to be equal to that of single-crystal material (galena). Electrode separation is about 2 mm and electrode length

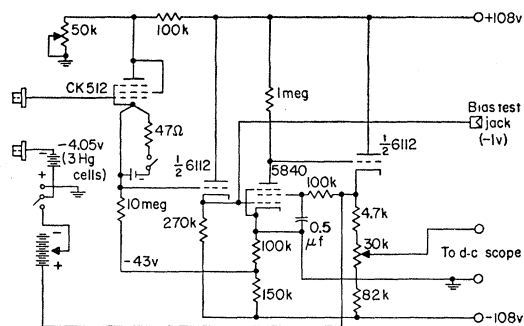


FIG. 5. Hi-Z dc amplifier.

about 5 mm. Since the film thicknesses are of the order of a few tenths of a micron, the cell resistance in ohms is roughly 10 000 times the reciprocal of the conductivity in  $(\text{ohm-cm})^{-1}$ .

PbS films show ohmic behavior whether in the dark or illuminated regardless of temperature, provided only that the applied electric field is not too high. Below 500 volts/cm all are ohmic in behavior. This is the case even at fields of only a few tenths of a volt per cm. In all the work to follow, all applied electric fields are less than 500 volts/cm, and in most cases are  $22.5/0.2 = 112$  volts/cm.

## EXPERIMENTAL RESULTS

### Variation of Dark Conductivity with Temperature

Figure 6 shows plots of logarithm of the dark conductivity,  $\sigma_D$ , vs reciprocal of the absolute temperature,  $1/T$  for some of the PbS films that were measured. For a simple, intrinsic semiconductor, the conductivity would obey an equation of the form  $\sigma = \sigma_0 \exp(-\Delta E/kT)$ , where  $\sigma_0$  is a constant, and such a plot would be a straight line having a (negative) slope of  $(-\Delta E/k)$ . On the figure, the numbers at the right of the curves are the cell numbers, and the percent figure in parentheses is the percent oxidant used to make the films. On subsequent figures, the values of slopes of straight-line portions of  $\sigma-T$  curves have been used to calculate the energy difference  $\Delta E$  which is expressed in units of electron volts.

Certain regularities in the data may be seen. Unoxidized films such as the 0% film No. 12 (although this is exposed to air during part of its processing) have high values of conductivity over all the temperature range from room temperature ( $1/T = 0.0034$ ) to liquid nitrogen temperature ( $1/T = 0.013$ ). As oxidation of the films increases, as indicated by the increasing percent values, conductivity decreases progressively until the range 20% to 40% is reached. Still higher percentages of oxidant generally result again in higher values of conductivity, and in curves which show smaller temperature coefficients of conductivity, i.e., the magnitude of the slopes of the curves is smaller.

The curves appear to approach an asymptote (the

dashed line) having a slope equivalent to  $\Delta E = 0.35 \pm 0.01$  ev. One cell in particular, No. 57 (called R57X in subsequent figures) lies right along this asymptote in the temperature range from 170° to 300°K. A number of other films, not shown, also approach the 0.35-ev slope. The few films which do cross over the line are without exception subject to the suspicion that the value of conductivity calculated is too low. Some are heavily oxidized films which do not have the smooth, mirror-like surface which less oxidized films have, and some are very thin ( $0.1 \mu$ ) and showed evidence of "burning off" near the electrodes so that their actual thickness may have been considerably less than that calculated from weight differences. With these exceptions then, all dark conductivity curves lie to the right of the line and asymptotically approach it as temperature increases.

### Effect of Substrate Material on the Conductivity-Temperature Curves

It has been suggested<sup>2</sup> that expansion and contraction of the substrate material on which a PbS film was deposited would noticeably alter the variation of film conductivity with temperature. If it were true that

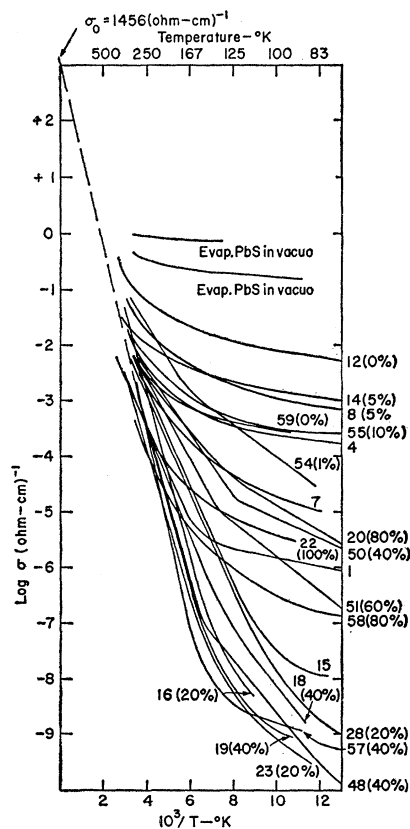


FIG. 6. Dark conductivity as a function of temperature for a variety of PbS material.

<sup>2</sup> R. A. Smith, Phil. Mag. Suppl. (Advances in Phys.) Suppl. 2, 325, 326 (July, 1953).

variations in contact resistances between crystallites, for example, were largely responsible for the variation, the energy gaps  $\Delta E$  in PbS films deduced from  $\sigma-T$  data would be considerably in error.

To check this important point, PbS films were deposited concurrently in one chemical bath onto substrates of glass and fused quartz. The dark conductivity was then measured as a function of temperature within a few days after the four cells had been baked in an oven. Results of these measurements are shown in Fig. 7. Since the coefficient of expansion of glass  $\approx 8 \times 10^{-6}$ , for fused quartz  $\approx 0.26 \times 10^{-6}$ , and for PbS (single crystals)  $\approx 18 \times 10^{-6}$ , the glass contracted almost 0.2%, for PbS twice this amount (if it is assumed the film behaves like a single crystal in this respect) and the quartz only 0.003%. Nevertheless, the conductivity curves for the four films are very nearly coincident. From these results the effect of substrate expansion with respect to a PbS film appears negligible. The spectral response and conductivity at different levels of irradiance similarly showed no differences which could be attributed to the two different substrates, although the latter property shows considerable variation from one film to another, even when the dark conductivity curves are very nearly the same.

The effect of the substrate material over a period of

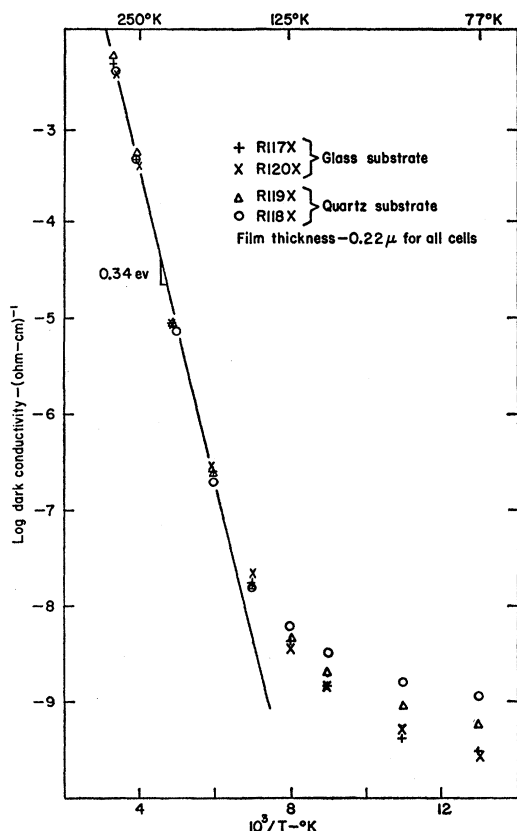


FIG. 7. Dark conductivity as a function of temperature for PbS films deposited on glass and quartz substrates.

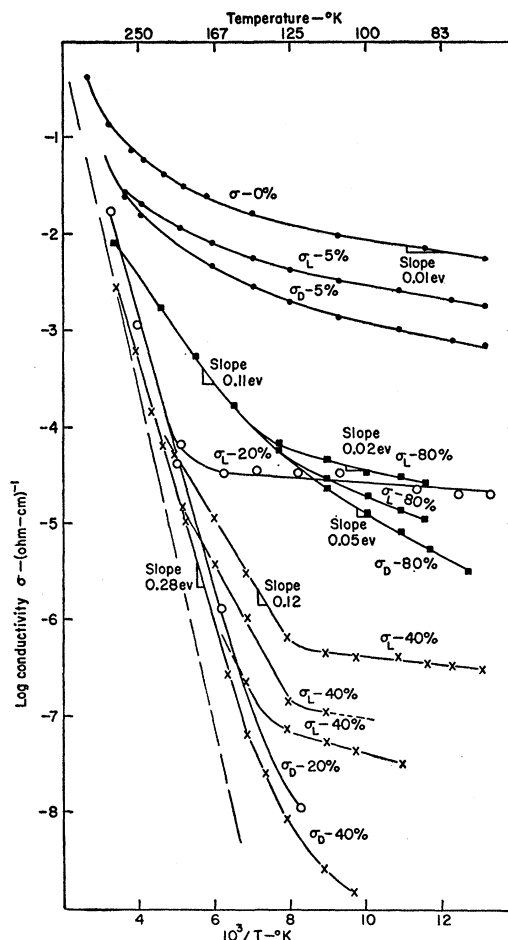


FIG. 8. Conductivity-temperature curves for chemically-oxidized films having various percentages of oxidizing agent in the chemical baths.

time was also checked and found to be negligible. Measurements of dark conductivity made five weeks later showed the dark conductivity had changed by less than a factor of three for any of the films. The largest changes occurred at low temperatures, while at high temperatures the change was less than 50%. Such good reproducibility and stability are not always obtained, but continual improvements in technique make this performance more and more likely. Second and third chemical depositions of PbS on glass and quartz substrates—four cells measured from each deposition—showed good reproducibility from deposition to deposition, though not as good as the cells made from one deposition. Experimental results check those of the first deposition rather well, with high-temperature slopes equivalent to  $\Delta E = 0.34$  eV for the  $\sigma_D-T$  curves.

#### Variation of Conductivity with Temperature and Irradiance

One of the first sets of data to show how conductivity of films changes progressively with temperature and

amount of oxidation is shown in Fig. 8. The 0% film is unoxidized except for any oxidation resulting from brief exposure to air at room temperature during processing of the film. When illuminated, no increase in conductivity was detected.

When 5% oxidant was placed in the chemical baths, conductivity in the dark, " $\sigma_D-5\%$ " in the figure, decreased about one decade, and some sensitivity to light was obtained as shown by the curve marked " $\sigma_L-5\%$ ." Amount of light on the film was uncalibrated in these early measurements, but was of course maintained constant for measurements on any one film. Further oxidation (20% film) resulted in a very great decrease in dark conductivity " $\sigma_D-20\%$ ," and a large increase in response of the film to light (the amount of light used for " $\sigma_L-5\%$ " and " $\sigma_L-20\%$ " are roughly comparable). A rather long straight-line portion is obtained for this film between the temperatures 150° and 300°K. The slope is 0.28 ev.

Greater oxidation using 40% oxidant caused a slight decrease in dark conductivity, " $\sigma_D-40\%$ " from that for the 20% film. The amount of radiation was not calibrated, but is substantially less than that used to obtain the " $\sigma_L-20\%$ " curve. Subsequent work showed that considerable variability in  $\sigma-T$  curves is obtained, but that about 20–40% oxidant always produced high-resistivity films having large response to light.

Still greater oxidation produces a large increase in dark conductivity, shown by the " $\sigma_D-80\%$ " curve in

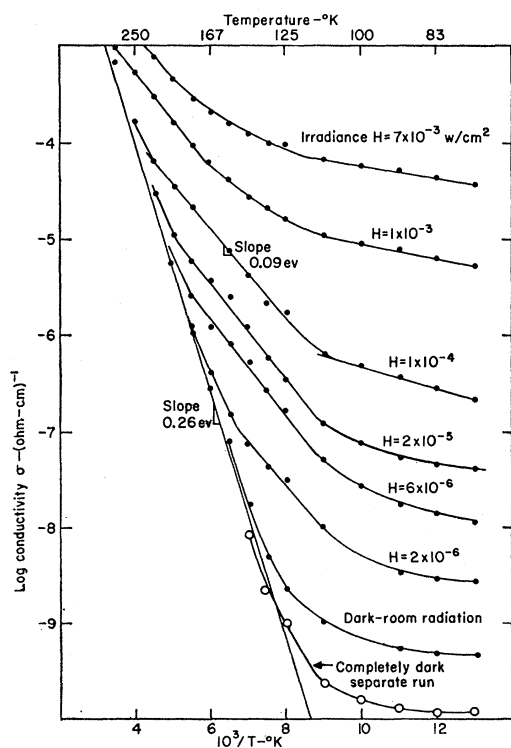


FIG. 9. Conductivity-temperature curves at various irradiances for cell R116X.

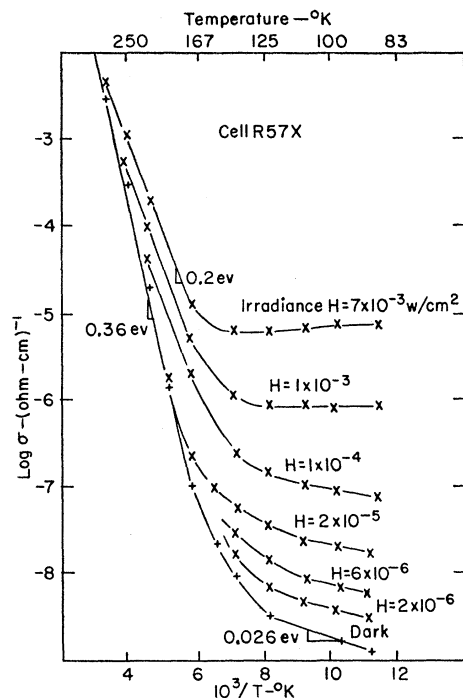


FIG. 10. Conductivity-temperature curves for a PbS film having maximum slope.

Fig. 8. Note the slopes of 0.12 ev at high temperatures and 0.5 ev at low temperatures. Two different amounts of radiation gave the " $\sigma_L-80\%$ " curves shown. Most remarkable is the way in which slopes of the  $\sigma-T$  curves at low temperatures decrease as illumination increases (from 0.05 ev in the dark to 0.02 ev for the higher level of illumination), and the way the  $\sigma_L-T$  curves join onto the  $\sigma_D-T$  curves as temperature increases. This latter effect means, of course, that the response to radiation,  $(\sigma_L - \sigma_D)/\sigma_D$ , is very much smaller at higher temperatures, not only because  $\sigma_D$  increases, but also because  $(\sigma_L - \sigma_D)$  decreases. The response  $(\sigma_L - \sigma_D)/\sigma_D$  is, of course, directly proportional to the signal voltage one will obtain across a load resistor  $R_L$  for the small signal situation, i.e.,  $(\sigma_L - \sigma_D) \ll \sigma_D$ .

One sees from Fig. 8 that there exists an optimum amount of oxidant if one is to produce a film of minimum conductivity. From experience one knows that films of minimum conductivity have about the maximum signal sensitivity; that is to say, the largest value of  $(\sigma_L - \sigma_D)/\sigma_D$  for unit irradiance. As nearly as can be seen from the figure, the optimum percentage of oxidant is 20%–40%. This checks out well with the dark conductivity *vs* temperature curves shown in Fig. 6 representing measurements on a large number of films.

Figure 9 shows data taken on a low-conductivity film with a calibrated tungsten lamp. The curves resemble those for cell R19X (the 40% film) shown in Fig. 8. The high-temperature slope of the  $\sigma_D-T$  curve (0.26 ev) is very nearly equal to that for R19X. The curve marked

"dark-room radiation" was taken with no radiation incident on the film except that from the approximate 300°K surroundings entering the aperture which admits the tungsten-lamp illumination. By closing off this aperture with metal in thermal contact with the cold reservoir surrounding the cell, the curve marked "completely dark" was obtained. A separate run is necessary to obtain these data as no practical cold shutter could be readily devised. Most films do not show such high sensitivity to room radiation as did this one, and it can be assumed that unless otherwise indicated the dark conductivity curves given for other films are substantially those one would obtain in complete darkness. At low temperatures, slopes of the  $\sigma$ - $T$  curves are small—order of 0.01 or 0.02 ev. This is observed for almost all films.

As was mentioned previously, a number of films have been made having at high temperatures a variation of dark conductivity with temperature equivalent to about 0.35 ev. The value 0.35 ev, it is to be emphasized, is the experimentally determined value of  $\Delta E$  in the equation  $\sigma = \sigma \exp(-\Delta E/kT)$  which for a simple semiconductor is equal to one-half the intrinsic gap  $E_g$ . A value for  $\Delta E$  exceeding  $0.35 \pm 0.01$  ev has not been observed experimentally, although about 100 films have been measured and deliberate attempts to produce a film having larger

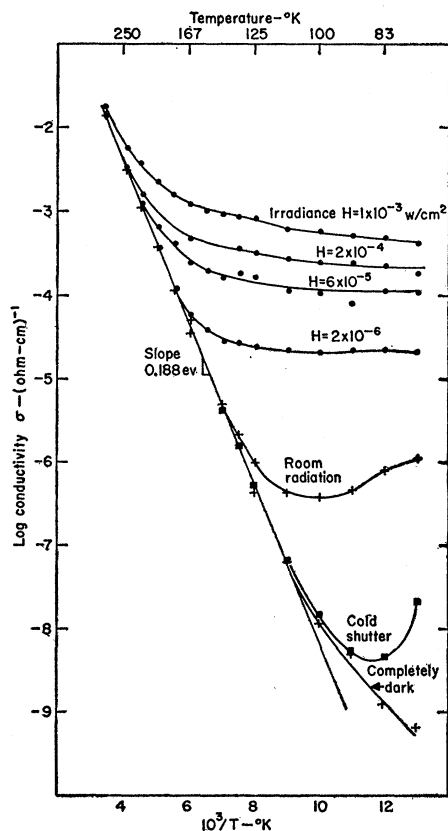


FIG. 11. Conductivity-temperature curves for Cell R114X—20% oxidizing agent.

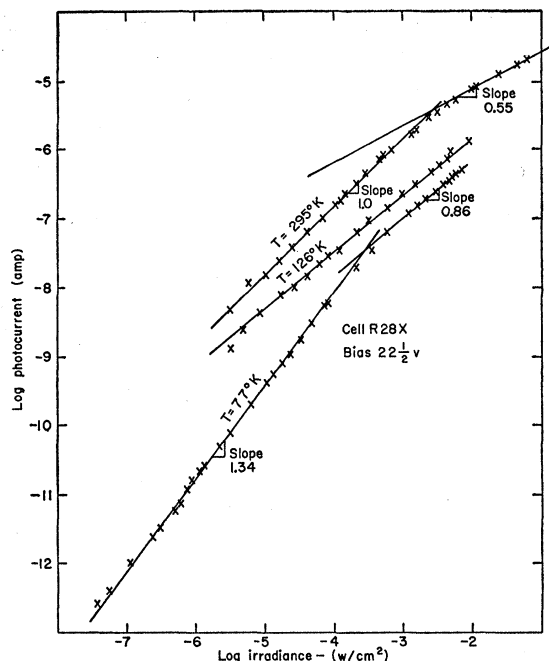


FIG. 12. Photocurrent as a function of irradiance for three different film temperatures.

$\Delta E$  have been made. Typical  $\sigma$ - $T$  curves at various irradiances for such a film are shown in Fig. 10. The slope of  $\sigma$ - $T$  curves at intermediate temperatures and sufficiently high irradiance is about 0.2 ev.

Figure 11 shows  $\sigma$ - $T$  curves which are rather unusual in that there is a pronounced upward curvature of the  $\sigma_L$ - $T$  curves at low temperatures and illuminations, resembling that commonly observed for the dark conductivity of bulk silicon and germanium. Similar upward-curving data are frequently seen for lead telluride films made at this laboratory. This film has an exceptionally high sensitivity when cooled; note the large response to room-temperature radiation entering the aperture in the apparatus (subtending at the cell about 0.03 steradian). In part this high sensitivity must be due to a spectral response which pushes out to exceptionally long wavelengths.

One other exceptional behavior for this cell is that photocurrent varies approximately as the square root of irradiance at low temperatures over unusually large ranges of temperature and irradiance.

One property which is always of interest theoretically is the manner in which photocurrent  $I_p$  [proportional to  $(\sigma_L - \sigma_D)$ ] varies with irradiance  $H$ . Figure 12 shows for one cell a plot of logarithm of  $I_p$  vs logarithm of  $H$ , so that a straight line of slope +1.0 represents a linear variation of  $I_p$  with  $H$ . For this cell, R28X, the photocurrent varies more rapidly than linearly. Such rapid variation has been observed for several cells at temperatures from 77° to 100°K. On the other hand, some cells have shown variations of photocurrent which are

substantially less rapid than linear (slopes as low as 0.5) at 77°K. At low temperatures, therefore, the photocurrent-irradiance characteristics have shown considerable variability. At higher temperatures, slopes of these plots lie fairly close to 1.0. At high irradiances—around 0.1 w/cm<sup>2</sup>—the slopes have approached  $\frac{1}{2}$  power for measurements on two cells.

At the present time it does not seem possible to make any generalizations about variation of  $I_p$  with  $H$ , particularly at low temperatures, except that no variation more rapid than linear has ever been observed at temperatures above 125°K. Cells have been measured whose  $\sigma_D$ - $T$  curves looked very similar to one another and yet the photocurrent-irradiance relationships were quite different. A specific case of this was cell R28X whose  $\sigma_D$ - $T$  curve resembled that for cell R114X (Fig. 11) quite closely. The dark conductivity curve was straight for about six decades in conductivity, with slope 0.17 ev, and the  $\sigma$ - $T$  curves under illumination broke sharply away from the  $\sigma_D$ - $T$  at low temperatures much as those for R114X do. Yet the photocurrent *vs* irradiance curves for this cell, shown in Fig. 12, are completely different from the square-root variation observed for R114X at low temperatures. The two sets of data,  $\sigma$ - $T$  and  $I_p$ - $H$ , are not related, therefore, in any obvious way. More sensitive films do show a tendency to a square-root variation at lower levels of irradiance than do less sensitive films. This is also our experience with PbS cells operating at room temperature.

#### Transient Response of Films

When a PbS film is irradiated with light which is square-wave chopped, the photocurrent does not in-

crease or decrease instantaneously but requires a definite time to rise or decay to the final values in the light and in the dark. The rise and decay have been found to be exponential if the ac response to the modulated light is not too large. This fact has been shown by numerous null-match measurements on a large variety of lead sulfide films.

Rise and decay times for exponentially-varying photocurrent are described by a time constant  $\tau$ , the amount of time required for the photocurrent to rise or decay the fraction  $(1-1/e)$  of its peak value where  $e$  is the base of natural logarithms. Rise- and decay-time constants are usually equal within experimental error, but for a few films some differences have been observed when the ac response due to the chopped light has been large. Decay times will be reported here, and except for measurements where the ac response is large it may be assumed that rise times are substantially the same as decay times. Since the time constant measured depends on the magnitude of the ac response, care must be taken to keep this at small values, usually less than 20%. However, as cell resistance becomes very large for certain cells when cooled, a good signal cannot always be obtained for use in the time-constant measurement without using ac responses larger than 20%, and these values are therefore more in doubt. Sensitivity of measured time constant to magnitude of the ac response varies considerably from cell to cell—sometimes an ac response of 100% makes no measurable difference in time constant. Where practicable, magnitude of the ac response,  $\Delta\sigma/\sigma$ , is shown in the figures.

Time constants have been found to depend only very

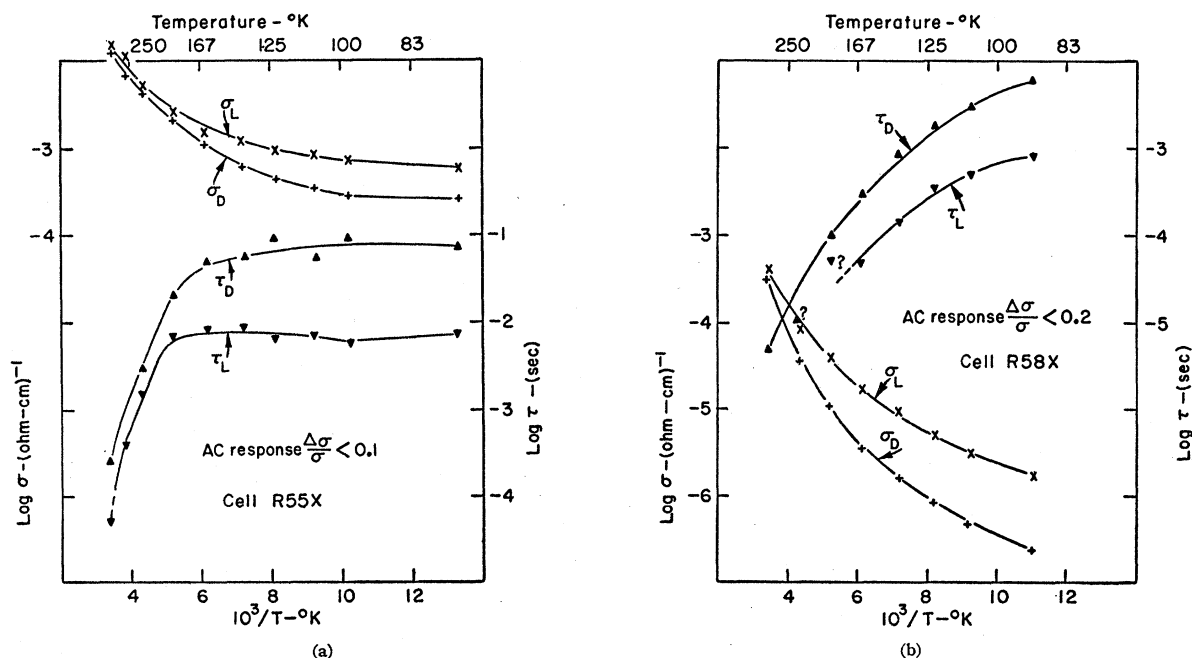


FIG. 13. Variation of time constants with temperature and film conductivity. (a) Cell R58X; (b) Cell R55X.



little on applied electric field and on wavelength of the radiation, although extensive measurements have not been made of these dependences. The time constant for any one cell depends very much on temperature and on irradiance. The latter may be varied in two ways. First, one can use an intense light source and square-wave chop all of this radiation. Second, one can irradiate the film with intense unmodulated light (background light) and superpose on this a weak square-wave-modulated light of only sufficient intensity to enable one to measure  $\tau$ . If the first method is employed, and a large ac response results (due to operation at low temperatures where response to radiation is large), the rise and decay curves are no longer simple exponentials. The second method enables one to select, by imposing appropriate background radiation, the value of conductivity at which time-constant measurements are to be made; then by keeping ac response small, the time constant measured is a simple exponential, characteristic of the chosen value of conductivity.

#### Variation of Time Constant with Conductivity

One may attempt to treat the large changes in  $\tau$  observed by changing temperature, and by application of intense unmodulated background radiation at low temperatures (where the dc response is large), as the variation of  $\tau$  with one variable only, namely conductivity of the PbS film. Figure 13 shows some data relating time constant and conductivity at different temperatures.

Consider first a simple case, shown in Fig. 13(a). The curve  $\sigma_D$  is the dark conductivity-temperature curve. The curve  $\tau_D$  is a time-constant *vs* temperature curve obtained by using a weak square-wave-modulated light to measure  $\tau$  at a value of conductivity very nearly equal to  $\sigma_D$ , i.e., if  $\sigma_L$  is the value of  $\sigma$  with the light on ( $\sigma_L - \sigma_D \ll \sigma_D$ ) and therefore  $\sigma_L \approx \sigma_D$  and  $\tau_D$  is the time constant representative of  $\sigma_D$ . The curve  $\sigma_L$  is obtained by irradiating the film with unmodulated light, upon which only a weak square-wave-modulated light is superposed to measure  $\tau$ ; therefore  $\tau_L$  is the time-constant characteristic of the conductivity  $\sigma_L$ . The  $\sigma_D$ - $T$  curve is very nearly a mirror image of the  $\tau_D$ - $T$  curve, as are the  $\tau_L$ - $T$  and  $\sigma_L$ - $T$  curves mirror images of one another. For this film, a heavily oxidized one (80% oxidant), the product  $\sigma_D \times \tau_D$  and  $\sigma_L \times \tau_L$  are constant with temperature and the two products are equal within the experimental errors.

A further illustration of how  $\tau$  may be reciprocally related to  $\sigma$  is shown in Fig. 14. Here, however, the temperature of the film (R114X, the  $\sigma$ - $T$  curves for which are given in Fig. 11) was fixed, and  $\sigma$  was varied by application of background radiation. The experimental problem in these measurements is to keep temperature low enough so that a large response to light is obtainable, and yet resistance low enough to permit  $\tau$  measurements under small ac response condi-

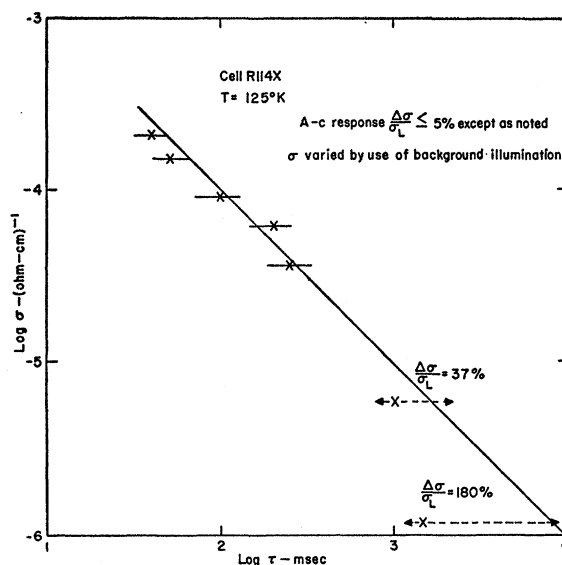


FIG. 14. Variation of time constant with conductivity at a fixed temperature.

tions. At the lower values of  $\sigma$ , a compromise had to be made—in order to obtain a clean signal, ac responses  $\Delta\sigma/\sigma_L$  exceeded 20% and one could expect the measured  $\tau$ 's to be too short. Within experimental uncertainty, then,  $\tau$  varies inversely with  $\sigma$  for this film at 125°K.

In general the simple relationship  $\tau \times \sigma = \text{constant}$  does not hold true. An example is shown in Fig. 13(b). These are data for a rather lightly oxidized (10% oxidant) film which was easily measured because cell resistance was low at all temperatures. Obviously, at high temperatures  $\sigma$  changes much less rapidly with temperature than does  $\tau$ . One also notes that a change in  $\sigma$  at low temperature by a ratio  $\sigma_L/\sigma_D$  of less than three produced about one decade change in  $\tau$ . Films for which  $\sigma_D$  changes rapidly with temperature show a relatively slow change of  $\tau$  over the same temperature range. This behavior is discussed further in a later paragraph.

Although there is a general tendency for the  $\sigma$ - $T$  and  $\tau$ - $T$  curves to be mirror images of one another, notable exceptions to mirror imaging occur as shown by the data in Fig. 15. In Fig. 15(a), the  $\tau_D$ - $T$  curve breaks quite sharply below 200°K and  $\tau_D$  appears to become almost constant at low temperatures. At high temperatures the  $\sigma$ - $T$  and  $\tau_D$ - $T$  curves are very nearly mirror images ( $\tau_D \times \sigma_D \approx \text{constant}$ ). Several other films having high-temperature slopes of  $-0.17 \pm 0.01$  ev for the  $\sigma_D$  curve have shown mirror imaging of the  $\sigma_D$ - $T$  and  $\tau_D$ - $T$  curves within experimental error. The  $\sigma_D$ - $T$  and  $\tau_D$ - $T$  curves shown in Fig. 15(b) are not mirror images over any temperature range measured. Slope of the  $\sigma_D$ - $T$  curve is  $-0.28$  ev, and the two slopes for the  $\tau_D$ - $T$  curve are about  $+0.17$  ev and  $+0.045$  ev.

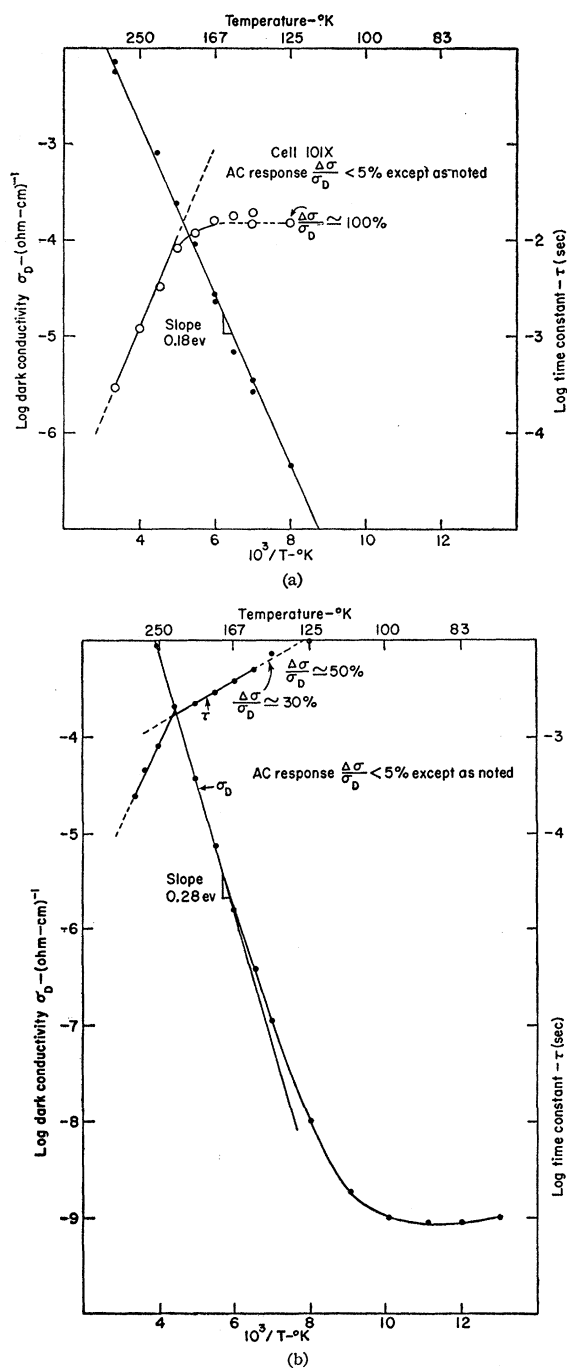


FIG. 15. Variation of dark conductivity and time constant with temperature for two high-resistance PbS films. (a) Cell 101X; (b) Cell R116X.

It was suggested by Gibson<sup>3</sup> that the logarithm of the ratio of time constant to conductance *vs* reciprocal of the absolute temperature was a straight line having an approximately constant slope of 0.35–0.40 eV for all cells

<sup>3</sup> A. F. Gibson, "A study of the decay of photoconductivity and other related properties in lead sulfide," Telecommunications Research Establishment, Memorandum No. 203 (unpublished).

at high temperatures. For a rather large percentage of the cells measured, this relationship has proven valid over a limited temperature range. Figure 16 shows some of the data of this kind with the further refinement that conductivity rather than conductance is used in taking the ratio  $\tau/\sigma$  (actually  $\tau_D/\sigma_D$  for most of the curves). One sees that not only is an approximately constant slope obtained (roughly  $\pm 0.3$  to  $0.4$  eV) but much of the  $\tau_D/\sigma_D$  data lie along a common line, with a few exceptions. Constancy of slope means simply that if one adds the *magnitudes* of the slopes of the  $\sigma_D$ – $T$  and  $\tau_D$ – $T$  curves, the sum is on the order of 0.3–0.4 eV in value. To put it another way, the more rapidly  $\tau_D$  changes with temperature, the less rapidly  $\sigma_D$  changes with temperature.

Re-examination of the data in Figs. 14 and 15 provides some support for the above relationship between  $\tau_D/\sigma_D$  and temperature over limited ranges of temperature at high temperatures where resistance is low and  $\tau$  is most easily measured under small-response conditions. A curve such as that for cell R116X, Fig. 15(b), obviously does not satisfy this relationship except perhaps over the intermediate temperature range where the slope of the  $\tau_D$ – $T$  curve is  $\pm 0.045$  eV. All that can be said now of the relationship illustrated by the data in Fig. 16 is that it correlates the time-constant and conductivity data for a considerable percentage of the cells measured (which includes about twice as many as are shown in Fig. 16) over a limited temperature range, even though the cells were prepared with greatly varying percentages of oxidant.

If the square-wave-chopped radiation is of high intensity and we have a sensitive cell which is cooled, then a large ac response is obtained and the decay of conductivity is not a simple exponential, but more rapid than exponential at the start of the decay.

Let  $\sigma(t)$  be the conductivity at time  $t$  after the start of decay,  $\sigma_L$  be the conductivity under steady illumination, and  $\sigma_D$  be the dark conductivity. Then for simple exponential decay:  $\sigma(t) = \sigma_D + (\sigma_L - \sigma_D) \times \exp(-t/\tau)$  and  $\ln[\sigma(t)/\sigma_D - 1] = \text{constant} - t/\tau$ . A plot  $\log_{10}[\sigma(t)/\sigma_D - 1]$  *vs*  $t$  for simple exponential decay would be a straight line of slope  $-0.434/\tau$ . Plots of this kind for the decay of conductivity with time have been made for several films. The films are operated at low temperatures and high light levels are used, so that response of the films to light is large. When the light is suddenly removed, the initial rate of decay determined from the differential slope of the plots may be ten times or more the final rate reached at long times, when conductivity has decayed almost to the dark value. The final rate of decay is the time constant,  $\tau_D$ , which one wishes to determine for small response conditions. If unmodulated background illumination is used to raise the conductivity to some value substantially larger than the dark value, the small ac response time constant  $\tau_L$  measured agrees roughly with the differential slope of

the conductivity decay plot at the corresponding value of conductivity, but accuracy of these measurements is not high.

The theory for PbS photoconducting films given in Slater's article on barrier theory<sup>1</sup> suggests that decay of conductivity with time be plotted as  $\ln \ln[\sigma(t)/\sigma_D]$  vs  $t$ . One such plot is shown in Fig. 17 for cell R114X. A plot for exponential decay of the kind discussed above gave a small ac response value of  $\tau_D = 0.25$  sec, in reasonable agreement with the value found from Fig. 17. The log-log type plots (as in Fig. 17) give straight lines over a greater range in time  $t$  than do the "exponential" type plots. The latter, in fact, had a slight curvature even though ac response was only 3%, making an accurate determination of  $\tau$  impossible. At higher temperatures where accurate measurements of  $\tau$  at small ac response are possible, rise and decay of photocurrent have been found to be quite accurately exponential as shown by the "null-match" type of measurements

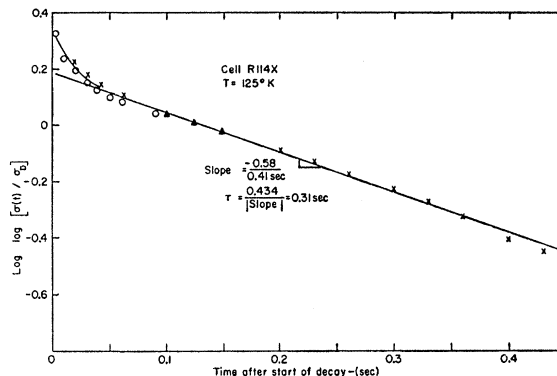


FIG. 17. Decay of conductivity with time for a large response to light.

discussed. At low temperatures where cell resistances are often very high and measurements correspondingly difficult, there is some question for the high-resistance films how accurately exponential are the rise and decay of photocurrent.

### Spectral Response of Films

The relative response of films to radiation of different wavelengths has been measured for numerous films at 77° and 296°K. Since the intensity of radiation in the monochromator beam is relatively low, and since the measurements are taken using radiation chopped at 10 cps, effects due to large changes in conductivity as a result of irradiating the films and due to time constant of the films are not important in these measurements. Precautions have been taken to minimize the effects of absorption in the glass cell windows (by the use of thin bubbles), and to eliminate frosting of any of the windows through which radiation must pass. The amplitudes of the response values are correct to within a factor of two for all the wavelengths covered (out to four microns).

Figure 18 shows spectral response curves for a rather large number of chemically oxidized PbS films. Logarithm of relative response is plotted against wavelength and the curves are normalized so that they coincide at  $\lambda = 1 \mu$ , a more or less arbitrary choice of wavelength. The ripples in the curves at the shorter wavelengths are due at least in part to optical interference effects in the films, since the films are a few tenths of a micron in thickness—of the same order as the wavelength of the radiation. Other experiments with film thickness as a parameter have shown that as the films are made thicker, the relative spectral response at long wavelengths (around  $2.6 \mu$ ) becomes larger and larger.

The ripples of the curves and the amount of sag due to variations in film thickness are of secondary importance theoretically. Of primary interest is the position in wavelength where relative response shows sharp drops. Casual examination of the data in Fig. 18 shows that there are edges where response drops sharply for

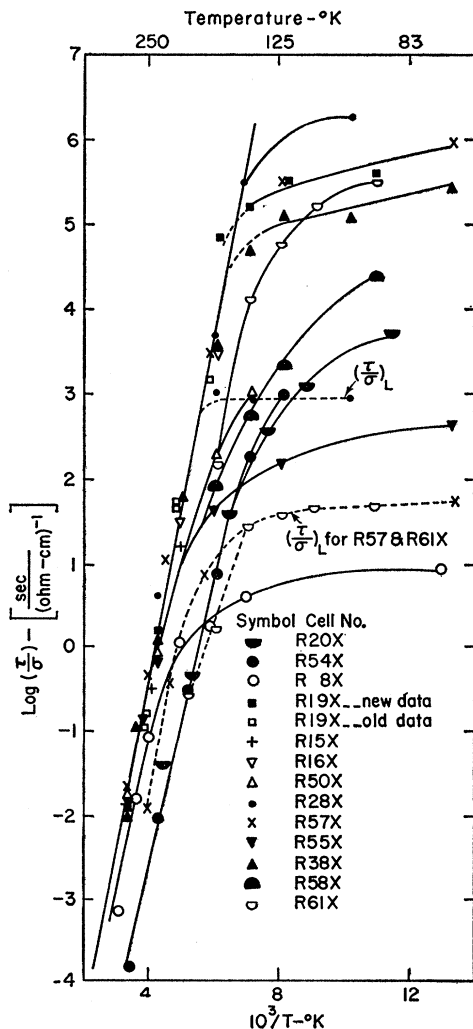


FIG. 16. Variation of the ratio (time constant/conductivity) with temperature.

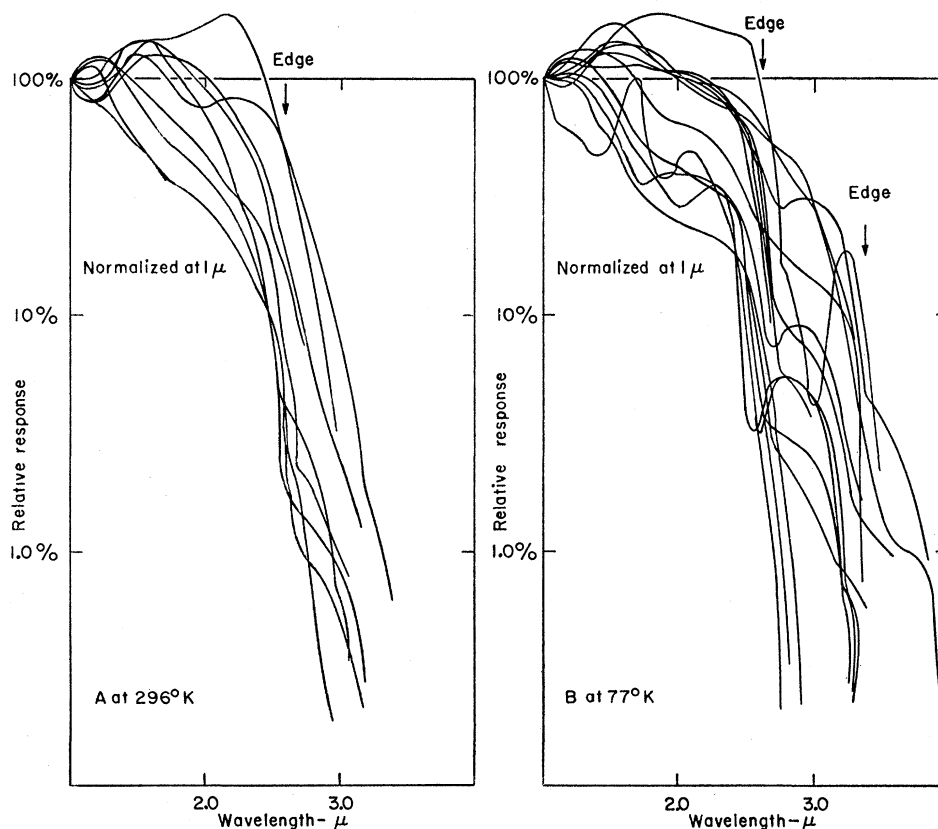


FIG. 18. Spectral response of PbS cells.

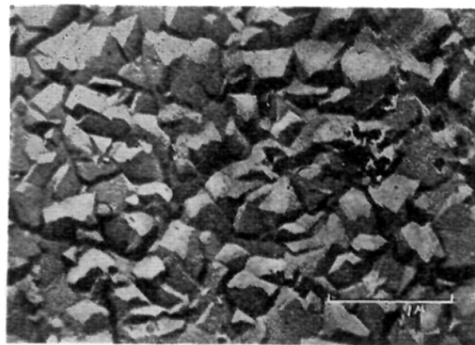
almost all films, and one can disregard the secondary influences of film thickness on the curves. At 296°K a distinct edge is seen at 2.6  $\mu$ ; 2.6  $\mu$  corresponds to about 0.48-ev energy. There is evidence of a second drop at around 3.2  $\mu$  (0.39 ev) at 296°K for a number of films. At 77°K the edge at 2.6  $\mu$  is still evident in most films, but a second distinct edge at about 3.4  $\mu$  (0.36 ev) is very evident, and for a very few films possibly a third at 3.9  $\mu$  (0.32 ev).

Experiments show that the hump lying between 2.6 and 3.4  $\mu$  in many spectral response curves at 77°K gradually develops as temperature decreases from room temperature. It is difficult to ascribe this phenomenon to absorption or interference effects. In fact there may be some correlation between the shape of spectral response curves and that of  $\sigma-T$  curves for a film, the latter being determined by how much oxidation the film has received. A very lightly oxidized film (0.1%), for example, showed no sharp drop in spectral response

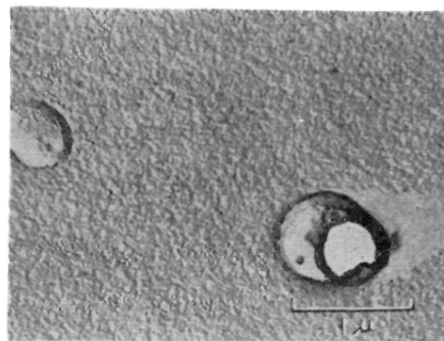
until 3.4  $\mu$ , while films having  $\sigma_D-T$  curves with large slopes often show exceptionally short-wavelength drops in spectral response, particularly at room temperature. A few high-resistance films have shown spectral responses which do not push out to longer wavelengths at all when cooled, even more than two decades down from the peak response. Three of these curves can be seen in Fig. 18.

#### ACKNOWLEDGMENTS

The writer wishes to acknowledge the valuable help of several members of Electronics Corporation of America, especially: Mr. Ronald Newburgh for his careful work on the chemically deposited films and the replication of these films for electron-microscope study; Mr. George W. Thelin for the design of a mechanical light chopper; Mr. Bradford T. Joyce for the design of the electrometer amplifier; and Mr. John McDonald for assistance with many of the experimental measurements.



(a)



(b)

FIG. 1. Electron microscope photographs of lead sulfide films.  
(a) Chemically deposited film; (b) chemically oxidized film.