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Final Report

THE CHEMICAL AND PHYSICAL STRUCTURES OF PbS FILMS IN RELATION TO PHOTOCONDUCTIVE SENSITIVITY

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I. SUMMARY

A study has been made of lead sulfide films with emphasis on relations between the method of preparation, physical and chemical composition, and photoconductivity. The two main features have been (a) an examination of particle size and orientation and of the chemical phases occurring as a function of the conditions of treatment, and (b) the relation of these compositional factors to the magnitude of the photoconductive sensitivity. The film composition was studied mainly by electron diffraction and microscopy, and the photoconductivity was measured in terms of the a-c signal developed across the d-c biased film when illuminated with interrupted "black body" radiation.

In the condensation of PbS on glass substrates, crystallite sizes can be readily controlled between 0.01 and 0.1 micron by adjusting the substrate temperature between 200° and 350°C. The crystallite orientation is substantially random. Variation of the condensation rate between 0.001 and 0.030 micron (film thickness) per second had only little effect on either particle size or orientation. Condensation on single crystal substrates produced single crystal films (on NaCl) or random orientation around particular zone axes normal to the surface (on diamond and MgO). Chemically deposited films show nearly random orientation of particles having sizes between 0.1 and 0.5μ which in photosensitive films occur in agglomerates of 2μ or more in diameter.

Three oxidized phases have been observed on heating condensed films in air: PbO (orthorhombic type), $PbO \cdot PbSO_4$ (lanarkite), and $4PbO \cdot PbSO_4$. In films exposed

to water the basic carbonate, $2PbCO_3 \cdot Pb(OH)_2$, occurs. In chemically deposited films (necessarily prepared in the presence of water) this basic carbonate is the only phase detected other than the PbS.

Photoconductive films with reproducible sensitivities were prepared by a particular process of condensation and subsequent oxidation. The following principal observations were made:

(a) The specific sensitivity could be reproducibly controlled in the range of 0.01 to 20 by the choice of the final temperature of oxidation in the range of 290° to 465°C.

(b) A correlated change occurred in the chemical composition of the surfaces. At the lowest sensitivity PbO had formed. At increasing temperatures of oxidation and sensitivity, $4PbO \cdot PbSO_4$ is found in increasing amounts until, for treatment at the highest temperature, the surface is completely covered with this basic sulfate.

(c) The photosensitivity can be influenced by a preliminary treatment of the PbS before evaporation and also by subsequent exposure of the oxidized film to the normal atmosphere, but neither of these factors affects the surface composition of the film as detected by electron diffraction.

The foregoing observations are not altogether consistent with current theories of photosensitive lead sulfide films and suggest the need for consideration of the correlation of composition and sensitivity in a restudy of the theoretical model.

II. INTRODUCTION

Interest in thin films of lead sulfide and also of lead selenide and lead telluride arose from the great change observed in their electrical resistances under the influence of incident radiation. The dependence of this photoconductive effect on the frequency of the incident light and on the temperature has made these lead compounds particularly adaptable as detectors of infrared radiation. Lead sulfide films show sensitivity up to about 3 microns wavelength, while the selenide and telluride films can be used to detect radiation up to 12 microns. These properties have led to the consideration of these films as infrared detectors in several applications; and they are reported to be superior to the conventional detectors in infrared spectroscopy.[1,2]

Many studies[3-7] have been made of the optical and electrical properties of the lead compounds in the hope of establishing a theory of the mechanism by which the absorption of radiation causes an increase in electrical conductivity. In the most comprehensive review of this work, Smith[7] deals extensively with electrical resistance as a function of temperature and the intensity and frequency distribution of the incident radiation, with the effect on these properties of variation in the methods of preparing the sensitive cells, with measurements of other physical properties including optical absorption and Hall effect, and finally with theories of the mechanism by which radiant energy may cause an increase in the number or mobility of current carriers. In this review only one paragraph out of forty-nine pages deals with the chemical and physical composition of photoconductive films.

The phases which are present in the film, their distribution relative to each other, and the particle sizes and orientations of the phases are dependent on variations in the procedures used in preparing the films. Because these properties of the phases together with the question of adsorption and diffusion of oxygen must form the connecting link between variations in the method of preparation and in the electrical and optical properties of the films, a systematic examination of relations between preparative procedure and film composition and between film compositions and photoconductivity is warranted. No such study has been reported, and the present study is directed along these lines for the case of partially oxidized lead sulfide films.

Previous work on the preparation of photoconductive lead sulfide films has not been reported in sufficient detail to serve as a reliable guide for obtaining films with reproducible properties, and it is necessary for any study of film composition to develop its own details of preparation. Two general methods of obtaining photoconductive PbS films have been used: (1) the chemical precipitation from an alkaline solution of lead acetate and thiourea,[8-11] and (2) the sublimation of lead sulfide in a vacuum chamber onto a glass substrate followed by heating in air or oxygen.[12-16] Whitcher[11] has reported that the chemical preparation of films of good sensitivity can be accomplished either by the Kicinski[9] method of adding sodium hydroxide solution to an aqueous solution of lead acetate and thiourea, or by the Oxley[8] method of adding thiourea to a strongly alkaline solution of lead acetate, although the results are highly sensitive to the concentrations and temperature of the solutions, the rate of addition and mixing, the presence of added electrolytes, and the subsequent treatment of the precipitated film. Cashman[12,13] has used the sublimation technique in the preparation of films in sealed cells; solid lead sulfide was preoxidized by heating in air or moist oxygen and then sublimed onto the window of the cell fitted with graphite electrodes. Cashman has told the present authors that the pre-oxidation step may be substituted by the use of a mixture of lead sulfide and lead oxide. Schwarz[15,16] carries out the evaporation in an atmosphere of oxygen. Other variations are known to be used in the commercial preparation of lead sulfide cells but the details have not been disclosed.

Some previous investigation of the composition of lead sulfide films has been done but never in correlation with systematic changes in the method of preparation or with changes in the observed photoconductive sensitivity. Phases other than lead sulfide have been reported in the X-ray diffraction examination of chemically precipitated films; traces of lead oxide and lead hydroxide are reported by Kicinski,[9] and lead oxide and a basic carbonate [designated as $PbCO_3 \cdot Pb(OH)_2$] are reported by James, Milner, and Watts.[17] Particle size in chemical precipitates of lead sulfide has been observed by Pick[18] in electron micrographs. Some evaporated films were reported from the laboratory of Lark-Horovitz[19] to show lanarkite ($PbO \cdot PbSO_4$) by electron diffraction. The most extensive work has been done by Wilman[20] using electron diffraction methods. He found only PbS in chemically prepared films but also observed in films less than 1 micron thick a tendency toward orientation with the (100) planes of the particles parallel to the glass substrate and an average crystallite diameter between 150 and 500Å. In some condensed films Wilman also found lanarkite, although a comparison by the present investigators of Wilman's published data with the more recently available data[21] on $4PbO \cdot PbSO_4$ suggests that this latter basic sulfate was present. Wilman concluded that photosensitivity in PbS films is related to slight deviations from the stoichiometric composition and the distribution of the oxidized phase among the PbS crystallites but not to the size or orientation of the crystals.

Most of the work previously reported for lead sulfide has been in the experimental measurement of its electrical and optical properties and in their interpretation in relation to theories of the mechanism responsible for photoconductivity in semi-conductors. The properties considered are the electrical conductivity at various frequencies, the Hall effect, the thermoelectric effect, the absorption spectrum, the photoconductive sensitivity and its dependence on temperature and spectral frequency and its response (decay) time. Most of the results are presented and discussed in Smith's review.[7]

The current carriers in PbS may be mainly either <u>n</u>- or <u>p</u>-type according to the occurrence of excess lead or of excess sulfur or oxygen.[22] Two principal values (1.2 and 0.4 ev) have been reported for the energy gap between the valence and the conduction bands in PbS as observed by Hall-effect measurements[23,24] and by optical absorption measurements.[25,26] The long wavelength limit for photosensitivity at room temperature coincides with the optical absorption edge at 0.4 ev.[26-28] The rapid decrease of electrical impedance with increasing frequency observed by Chasmar[29] was interpreted as evidence for the occurrence of high resistance-intercrystalline barriers in photoconductive films although the impedance variation can be accounted for without such barriers.[30,31]

Three classes of theories[32] have been proposed for the mechanism by which the absorption of radiation affects the number of or the mobility of electrical current carriers. The first proposes that photoconductivity is characteristic of intrinsic semiconductors or of those having equal numbers of <u>n</u>- and <u>p</u>-type impurity centers so that the absorbed radiation simply increases the number of current carriers. For PbS this is supported by the agreement between the lower value (0.38 ev) proposed for the energy jump between valence and conduction bands and the spectral limit of photosensitivity; but it is not consistent with the usually observed rate of decay of conductivity or the a-c resistance data. The second class of theories proposes the existence of potential barriers whose height is reduced on absorption of radiation whereby the mobility of carriers is increased. Specifically considered[14,33] is the formation of p-n junctions due to the absorption of oxygen in vacant sulfur sites and the subsequent redistribution of charge. Also suggested[34] is some type of surface states which trap "holes" on the surfaces of p-type crystals; any photoelectrons tend to neutralize the positive charge and thereby reduce the barrier opposing the flow of "holes." The barrier theories have been preferred[35] mainly on the basis of the data on the rate of decay of conductivity and its dependence on temperature and intensity of illumination. The third class of theories[36] postulates the existence of impurity centers which reduce the required excitation energy; this theory is more plausible in the form proposed by Rose[37] who postulates that electrons trapped by centers lying in the forbidden band can return to the valence band only by way of the conduction band. On this basis Rose discusses the observed photosensitivity and decay rate in terms of the concentration and distribution of trapping centers and criticizes the postulate of p-n barriers in the previous theory.

III. STATEMENT OF PROBLEM

The variations in the structural features of photoconductive films implied in the theoretical speculations mentioned above made it seem desirable to have more precise information on the physical and chemical composition of lead sulfide films. Such a study offered more significant results if they could be correlated in any way with the observed photoconductive sensitivity.

Because of the proposals regarding the role of barriers in photoconductivity, attention was first given to achieving a variation in the number and total area of interphase contacts among the film particles by varying the particle sizes and relative orientations. Specifically, this included the use of glass and of single-crystal substrates with systematic variations in the temperature and time of laying down the PbS, especially in the vapor condensation method. The subsequent sensitization by oxidation of the film to achieve reproducible photoconductivity was then given detailed attention in the evaporated films. The identification of crystalline phases and determination of their orientation was done by electron and X-ray diffraction. Electron micrographs were prepared for determination of particle size and distribution of phases. Photoconductive sensitivity was observed using interrupted illumination and a tuned a-c amplifier.

A less intensive study of chemically deposited films was made because of the much greater difficulty in obtaining reproducible high sensitivity; the larger number of variable factors in the preparation made it not feasible to rediscover the undisclosed favorable recipes with a reasonable expenditure of effort. A limited number of chemical films of moderate sensitivity were prepared and examined; two sets of commercial films having "high" and "low" sensitivity were examined by electron diffraction and microscopy.

The present report describes the essential features of the experimental procedures and results, but many manipulative details and observational results having no apparent significant bearing on the behavior of photoconductive films have been deleted for the sake of brevity.

IV. EXPERIMENTAL PROCEDURES

The basic requirement of this work was the preparation of lead sulfide films under a variety of controlled conditions, with ultimate emphasis on the preparation of films of reproducible photosensitivity. For this reason the principal experimental procedures need to be carefully defined, and the treatments involved in preparing the substrates, depositing and treating the films, and their subsequent examination are described in the following paragraphs.

A. PREPARATION OF SUBSTRATES

The condition of the surface of the substrate influences the deposit laid down on it. The two principal substrates were cleaned and their physical state examined by electron microscopy and diffraction.

Most of the lead sulfide deposits were made on glass surfaces. Flat sections were used to allow full access for examination by diffraction and replica methods. Sections of 8 x 25 x 1.0 mm were cut from the best grade of chemically resistant microscopic slides; they were cleaned in a hot detergent solution followed by immersion for 15 minutes in a chromic-sulfuric acid cleaning solution, by rinsing in a stream of distilled water at 60°C discharging directly from the block tin condenser of the still, and by drying at 125°C in a dust- and grease-free oven.

Examination by electron diffraction and microscopy showed that the surface of the glass was devitrified to a depth of the order of 100Å but that any surface irregularities had diameters and depths of less than 100Å. The devitrification produced crystalline particles of no more than about 50Å in size and with random orientation, and this was expected to offer no epitaxial effect on the condensed lead sulfide. This devitrification was observed on all glass microscope slides examined. It was not produced by the action of the acid cleaner since treatment in very clean organic solvents also led to the same crystalline diffraction pattern, although the slightest trace of grease (corresponding to a monolayer on the surface) was enough to obscure the crystalline pattern. The devitrification evidently is a result of aging of the glass and undoubtedly occurs on all glass slides but is ordinarily not detected.

In a number of experiments the (100) faces of sodium chloride crystals were used as monocrystalline substrates. Large specimens obtained from The Harshaw Chemical Company were cleaved into sections of about 8 x 25 x 3 mm. The cleaved surfaces were rubbed gently on a moistened Buehler Miracloth stretched on a flat block and polished lightly on 4/0 emery paper. The polishing debris was removed by etching in a stream of tap water for two or three seconds followed by drying in absolute ethyl alcohol and a stream of dry air. The electron micrograph of a replica shows occasional regular etch pits up to 0.2 micron in size on an otherwise smooth and uniform surface. The electron diffraction pattern of the crystal indicates the absence of strain in the surface layers and of any misoriented material. Heating the crystals to the temperatures used in preparing the PbS films showed no effect in the micrographs and diffraction patterns of the cooled crystals.

For electrical measurements on the deposited films, the substrates were first provided with graphite electrodes. On each end of the glass a dilute aqueous suspension of colloidal graphite was evaporated to give a light coating over a length of about 6 mm. On the sodium chloride a suspension of graphite in isopropyl alcohol was used. Electrical contact was made through the mounting clamps.

B. PREPARATION OF LEAD SULFIDE FILMS

The films condensed from the vapor were prepared with the aid of the specimen holder shown in Fig. 1. The base plate is monel metal of 2 x 3/4 x 1/8 in. The nichrome heater is wound on a mica support carried on ceramic posts. One specimen clamp carries a thermocouple for measuring the temperature of the specimen; the two clamps provide connections to the measuring circuit.

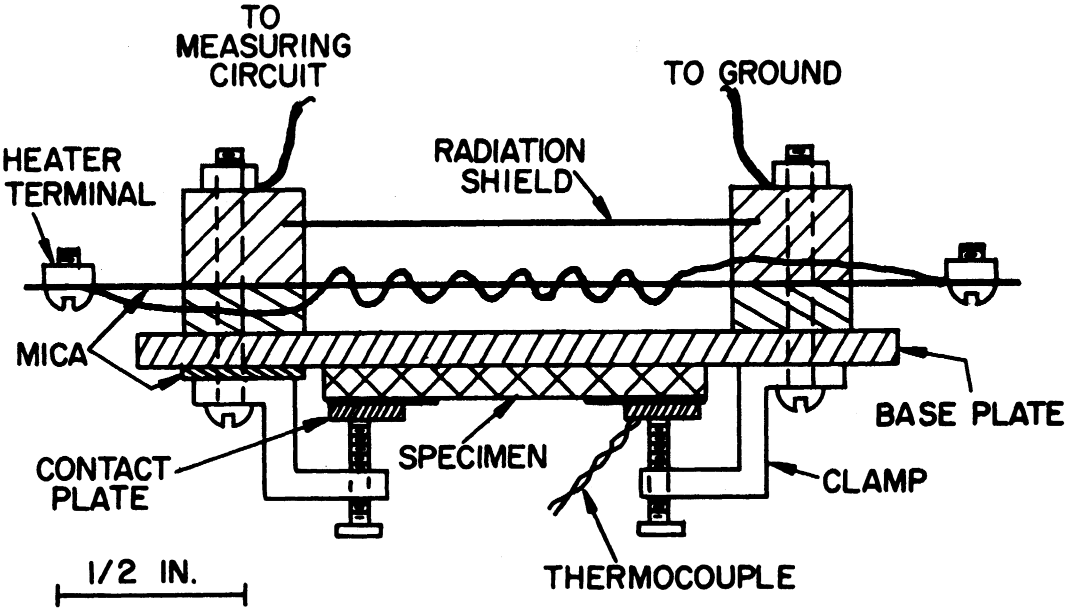


Fig. 1. Specimen heater and support.

The specimen support was mounted under the bell jar of a Model SC-3 Vacuum Evaporator Unit (Optical Film Engineering Company) and electrical connections for the heater, the thermocouple, and the specimen were made through six insulated posts in the base plate. The specimen was positioned so that the interrupted radiation could reach it in the photosensitivity tests. A Vycor cup of 1/4-in. diameter and 1/2-in. depth was mounted 6 in. below the specimen surface; an electrical heater controlled the temperature of the cup for evaporating its charge of lead sulfide. A metal shutter was mounted between the evaporating cup and the specimen, and a mechanical displacement of the shutter provided control of the flow of vapor. The other modification of the evaporation unit was the insertion of a liquid nitrogen trap between the diffusion pump and the base plate and the attaching of a system for admitting measured volumes of oxygen or air to the bell jar.

The basic procedure consisted of charging the cup with about 100 mg of PbS, reducing the chamber pressure below 10^{-4} mm Hg, and heating the evaporating cup to outgas the charge while the shutter is closed. When the pressure has fallen to the original value, the specimen is raised to the desired temperature, the cup temperature is raised to about 730°C (corresponding to a PbS vapor pressure of 0.02 mm Hg) and a steady flow of vapor is produced and controlled by the mechanical shutter. Under these conditions the film is deposited on the specimen surface at the high rate of 0.03 micron per second as determined on a microbalance. Subsequent cooling of the cup, adjusting the temperature of the specimen, and admitting controlled volumes of oxygen allowed treatment of the PbS film at any desired temperature and pressure of oxygen.

The first procedure which was successful in giving films of fairly high and reproducible photoconductive sensitivity involved building the film up in successive layers each of which was oxidized before the condensation of the next layer.

The details are given because this procedure was used in the long series of films showing a correlation between photoconductivity and chemical composition.

(a) A 0.1-micron layer of PbS is condensed on the substrate held at 290 ± 5°C. The d-c resistance of the film gives a rough but rapid indication of thickness.

(b) The cup heater is disconnected. Dry air to 0.5 mm Hg pressure is admitted either immediately or after 30 seconds. The temperature of the PbS supply in the evaporating cup is thus either 730°C or 530°C when the air strikes it; in the first case an appreciable pre-oxidation occurs on the surface of the powder prior to the next evaporation.

(c) After 3 minutes the chamber is pumped out.

(d) The cycle of steps (a), (b), and (c) was repeated until seven layers were laid down and oxidized. The composite film was then given a final heating at a temperature which was varied between 290°C and 465°C but only for the time required for the substrate heater to reach the desired temperature (no more than two minutes). The film was cooled to room temperature in the presence of 0.5-mm pressure of air.

The only variations made in this principal series were the temperature of the final treatment and the pre-oxidation or not of the PbS supply.

Another procedure was later discovered which gave good sensitivity without using successive layers. A supply of PbS powder was pre-oxidized by heating in an oven at atmospheric pressure and 500°C for 15 minutes. This powder was then evaporated onto a glass substrate at 290°C to give a layer about 0.2 micron thick. Dry air was admitted to a pressure of 1 mm Hg, and during 20 minutes at 290°C the air was renewed five times by pumping down below 10^{-3} mm and recharging the chamber to 1 mm. Finally the film was heated at the same air pressure during 15 minutes to 465°C, cooled to room temperature, and dry air admitted to one atmosphere.

A number of chemically precipitated cells were prepared using the general procedure described by Kicinski,[9] in which NaOH solution is added to a solution of thiourea and lead acetate. Preparations were made at various concentrations of solutions and at temperatures of 0°C, 20°C, and 55°C. The photosensitivity results were erratic for all the procedures used, and no one detailed procedure can be recommended.

C. MEASUREMENTS OF PHOTOCONDUCTIVITY

After a preliminary period of testing during which the proportional change in d-c resistance on illumination was observed, a standard method suitable for films of widely varying sensitivity was adopted on the recommendation of Dr. K. N. Tanner of the Naval Ordnance Laboratory, Corona.

The cell (film on its substrate with attached electrodes) was connected in series with a resistor chosen to have nearly the same d-c resistance as the cell and with a fixed d-c bias potential. For films of the condensed type connections were made through the base plate of the vacuum evaporator unit so that the photosensitivity and the resistance could be observed at various stages in the preparation of the cell. The radiation falling on the cell was taken from a calibrated tungsten source and passed through a rotating notched wheel which provided interruptions at 510 cps. The interrupted illumination of the cell produced an a-c potential which was connected through a cathode follower to an amplifier for display as a meter reading or on a cathode ray oscilloscope.

The amplifier used was the six-stage Hewlett-Packard Model 415A Standing Wave Indicator, which incorporated a twin-T feedback filter network tuned to 510 cps with a band width of approximately 25 cps. The output meter was calibrated to read directly in terms of a-c voltage generated by the cell and covered ranges from 10 microvolts to 10 volts full scale. The oscilloscope was the Dumont Model 304A with the Hewlett-Packard Model 450A preamplifier. The cabinet housing the load resistors and the bias supply also contained multirange voltmeter and microammeter for determining the d-c resistance of the cell.

The illumination was supplied by a 6-volt, 9-ampere General Electric Recorder Lamp (9/T 8 1/2 16) having the straight ribbon tungsten filament. This source approximates a black-body distribution over a wide temperature range; the calibration supplied is shown in Table I. All the quantitative measurements of cell response were made with this "black-body" source used at 30 cm and at specified color temperatures. While the sensitivities reported are not on a trustworthy absolute scale, the relative values from various cells are satisfactory for comparison purposes. The interrupter was an aluminum disc having 17 equally spaced radial slots

TABLE I

CALIBRATION OF GE RECORDER LAMP

Filament Current, amp	Color Temperature, °C	Flux Density at 30 cm μ watts cm^{-2}	Equivalent Black Body Radiation Peak, μ	 50% of Energy Below μ	 90% Below μ
3.6	800	58.5	2.68	3.8	8.7
3.8	1000	67.5	2.26	3.2	7.3
4.9	1500	198	1.64	2.3	5.4
7.1	2000	855	1.27	1.8	4.1
8.4	2180	1800	1.18	1.67	3.8

and was rotated at 1800 rpm; 52% of the lamp radiation was passed by this interrupter. The whole area of the cell under test was illuminated and local variations over the surface of the cell were not detected in the measurements made in this laboratory.

The sensitivity measurements are reported in terms of the specific sensitivity, S_1, defined by the equation

$$S = S_1VFM$$

where

S = a-c signal in microvolts

S_1 = specific sensitivity in microvolts per volt bias per microwatt cm^{-2} radiant intensity

V = d-c bias voltage

F = intensity of illumination in microwatts cm^{-2}

M = mismatch factor

For the present purpose of comparative measurements the bias was maintained at 15 volts. Values of F in the neighborhood of 100-200μ watts cm^{-2} were often used, this figure having been corrected for attenuation by the interrupter and by the wall of the vacuum bell jar, when appropriate. The mismatch factor, M, was kept within 5% of unity by appropriate choice of the load resistor value for each cell tested.

The noise voltage (signal observed from the biased cell without illumination) was nearly always observed and recorded but without reporting the noise equivalent power in more than a few cases. Some observations were made on response time with the aid of the oscilloscope. It became evident after some study of the sensitive films prepared in this investigation that the specific sensitivity was the property of first interest in relation to changes in the structure of the film and the results are presented and discussed in relation to this property.

D. ELECTRON AND X-RAY DIFFRACTION

Diffraction techniques were used for identifying crystalline phases, for extimates of the relative amounts of phases, and for studying the nonrandom orientation in both polycrystalline and single-crystal films. Electron diffraction was always used on the films because of its greater sensitivity to minute amounts of material. The considerations involved in the interpretation of electron diffraction data have been discussed in detail.[38-40]

The lead sulfide films on glass could be studied only by the reflection technique with the beam incident at an angle of 1-2°. The diffraction pattern is characteristic of a layer only 30 to 50Å thick when the surface is very smooth (i.e., protrusions of no more than about 10Å). On rougher surfaces ridges up to about 1000Å in thickness may be penetrated, but the possibility must be recognized that any material which is located only in the valleys on such a rough surface may not be reached at all by the electron beam. For this reason the interpretation of the reflection electron-diffraction patterns was always monitored by the examination of the surface contours appearing in the electron micrographs of surface replicas.

The transmission technique in electron diffraction was applied to the PbS films on sodium chloride crystals. The specimen was prepared by flowing a solution of collodion in amyl acetate over the film to act as a support which makes no contribution to the diffraction pattern because of the noncrystallinity of the collodion. The composite collodion-PbS film was removed from the substrate by dissolving the NaCl in water. One portion of the film was then washed in distilled water and mounted on a wire gauze for examination by transmission of electrons in both electron diffraction and electron microscopy. Another portion of the composite film was treated with nitric acid for removing the PbS; the remaining collodion replica was then examined in the electron microscope in an examination of the surface contours of the original PbS film.

The technique of diffraction by transmission was also used on some chemical preparations of PbS films. Thin collodion films (about 0.1 micron) were cast on water and then pressed onto a glass microscope slide which already carried several 1/8-in.-diameter-wire specimen screens. This slide was then immersed in a solution in which the chemical precipitation was performed so that crystal growth occurred directly on the collodion surface. This technique made it possible to examine chemically prepared films by direct transmission in both microscopy and diffraction.

The electron diffraction equipment used here was the standard RCA unit, Model EMD-2. The accelerating potential was 50 kilovolts, and the beam diameter on the specimen could be adjusted between 0.2 and 3 mm. The charging effect on reflection specimens mounted on glass was compensated by an auxiliary spray of electrons of about 500 volts energy, although this required precautions to prevent the deposit of a very thin film of decomposed pump oil on the face of the specimen.

X-ray diffraction was also used in the attempt to identify oxidized phases on specimens which had been heavily oxidized. On mounted PbS films the standard reflection methods were applied, including the high-angle "back-reflection" technique. The conventional techniques of X-ray diffraction from powders were used on bulk specimens of PbS powder which had been oxidized.

E. ELECTRON MICROSCOPY

The techniques of electron microscopy are well known.[41-42] The methods used in this study for preparing specimens will be described.

Because the films on glass could not be removed intact and often were too thick for electron transmission, replicas of the surface were prepared. A thin film of collodion was formed on the surface and the "dry-stripping" method of separating the collodion with cellophane tape was successful when the surface was not too rough.

For rough surfaces the "wet-stripping" method was used with the aid of dilute nitric acid. One end of the glass slide is dipped into the acid solution so that the acid reaches the collodion-PbS interface while keeping the upper surface of collodion dry. As the PbS dissolves, the collodion comes free and floats on the solution on slow immersion of the glass slide. Specimen support gauzes are laid on the top of the replica, and, after washing, the sections are dried and examined in the microscope. Because this technique destroys the PbS specimen, it could not be used when other types of examination were also required.

"Positive" replicas were sometimes prepared. A thick film of Acquanite "A" resin is formed on the surface. This resin is very tough and can be removed without tearing. The replicated side of the resin film is then covered with a thin layer of Formvar by evaporating several drops of an ethylene chloride solution (0.5-1% by volume). In amyl acetate the Acquanite dissolves, leaving the Formvar replica for mounting and examination.

Replicas prepared by any of the foregoing methods were always treated in two additional steps. Spherical particles of polystyrene latex of 0.26-micron diameter were deposited on the replica from a very dilute suspension in water. Palladium metal was "shadow-cast" onto the replica to increase the contrast and show the relief on the surface.

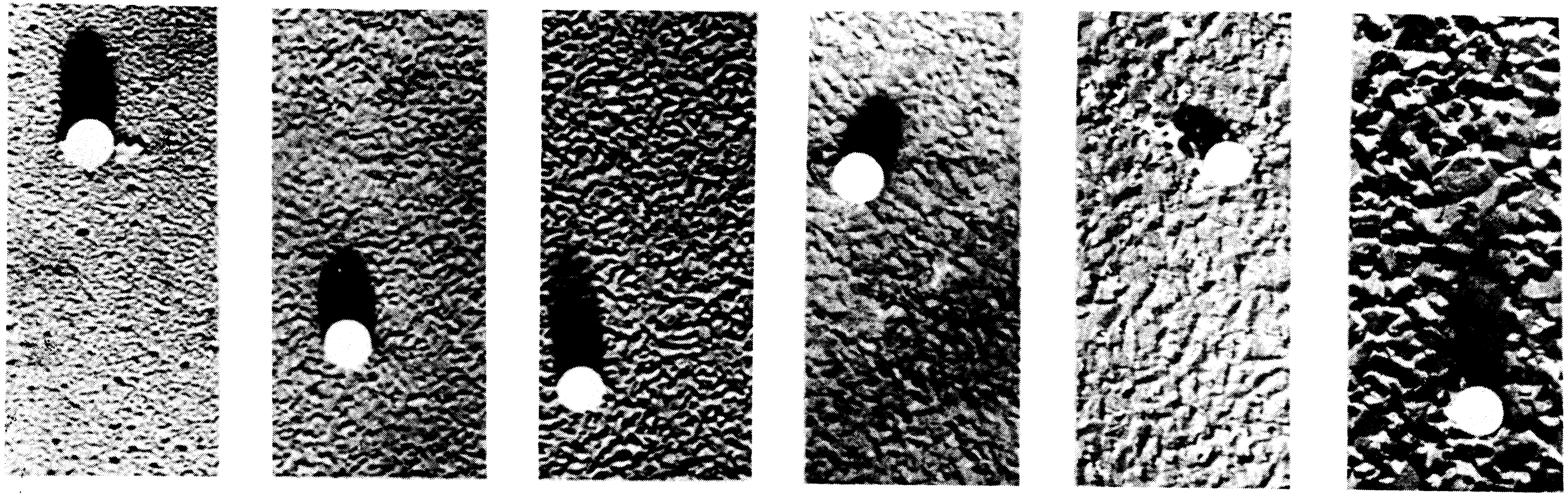
The RCA Model EMU-2A microscope was used in making the electron micrographs.

V. EXPERIMENTAL RESULTS

A. EVAPORATED FILMS ON GLASS

1. Composition of Unoxidized Films.—Films on glass were studied first to determine the particle size and orientation in relation to the temperature of the substrate during condensation and also to the temperature during subsequent heating. Later the effect of pre-oxidation of the PbS powder was studied, and effects of the evaporation on the film composition were sought.

For examining the effect of substrate temperature, several series of films on glass were prepared by complete evaporation of a 4.5-mg sample of PbS powder (without pre-oxidation) over a 3-minute period while maintaining the chamber pressure below 10^{-4} mm. The final film thickness was approximately 0.15 micron. The substrate temperatures in the series ranged from 200° to 350°C. The typical micrographs in Fig. 2 show crystals with nearly random orientation ranging from less than 0.01μ at 200°C to about 0.1μ at 350°C. Higher substrate temperatures were not tried extensively because re-evaporation of the film began above 350°C and because the particle size of 0.1μ achieved between 300° and 350°C corresponded to the particle size observed in the preliminary examination of commercial films of good photosensitivity. For this latter reason in the later study of photoconductive films on glass a temperature near 300°C was chosen for the initial condensation.



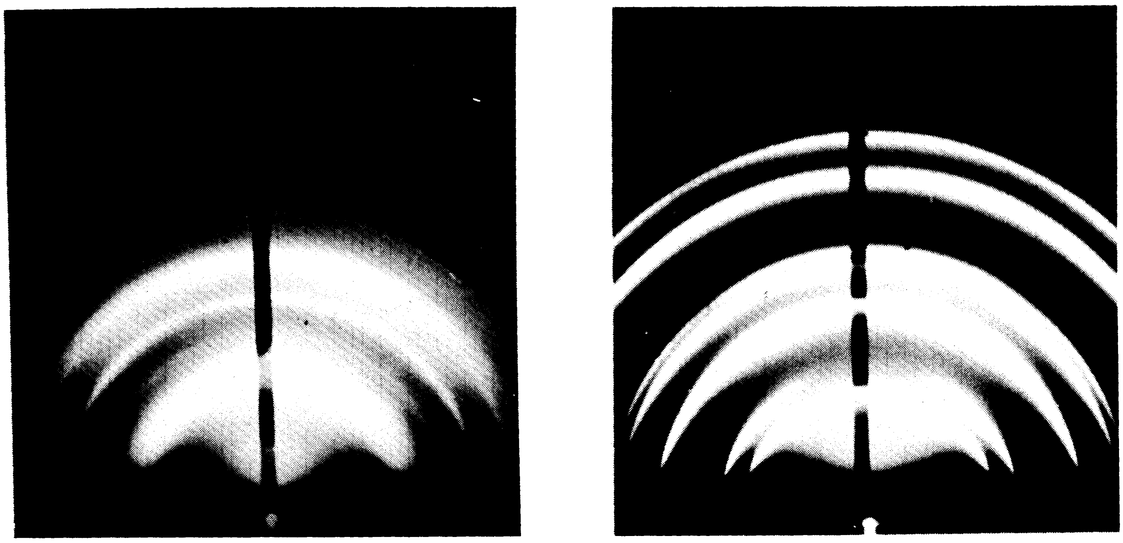
a. 200°C b. 250°C c. 275°C d. 300°C e. 325°C f. 350°C

Fig. 2. PbS films condensed on glass (electron micrographs—25,000X).

The effect of aging was observed by holding films at the temperature of condensation in the evacuated chamber for up to three hours at 200°C, up to two hours at 300°C and up to one hour at 350°C. The resulting micrographs show only a moderate increase in average particle size but a more pronounced tendency toward prepared orientation. At 300°C the (111) planes of PbS show a preference for being parallel to the substrate; in some cases at 350°C the (100) planes were more nearly parallel to the glass base.

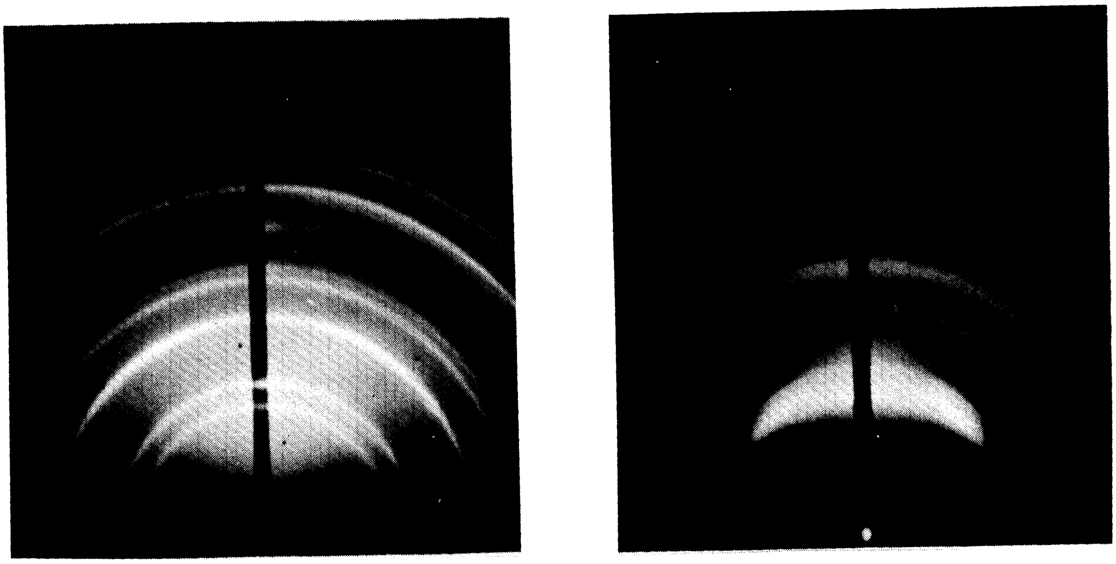
The electron-diffraction patterns of these films show mainly the maxima due to crystalline PbS (Fig. 3). The increase in crystal size and in the tendency toward preferred orientation appears in the comparison between the film condensed at 200°C (Fig. 3a) and at 350°C (Fig. 3b). A notable feature of the diffraction patterns is the appearance of extra rings (in addition to those of PbS) from films condensed in 3 minutes at 200°C (Fig. 3a) or condensed in one minute at 350°C (Fig. 3d). When the 200°C film was aged for 30 minutes all extra rings disappeared and the remaining pattern (Fig. 3c) corresponds to PbS in a clear and sharp fashion. The 350°C film after three minutes has the crystalline PbS much better developed and does not show the extra lines of the one minute film (Fig. 3b and d). The appearance of the extra diffraction lines in the freshly condensed films and their disappearance on aging at the temperature of condensation led to an extensive study of the electron and X-ray diffraction patterns of PbS powder before and after evaporation.

The PbS powder before evaporation was examined both before and after "pre-oxidation" treatment given by heating in air at various temperatures, pressures, and times. (Certain pre-oxidation treatments had been suggested previously as



a. 200°C, 3 min

b. 350°C, 3 min



c. 200°C, 30 min

d. 350°C, 1 min

Fig. 3. PbS films condensed on glass (diffraction patterns).

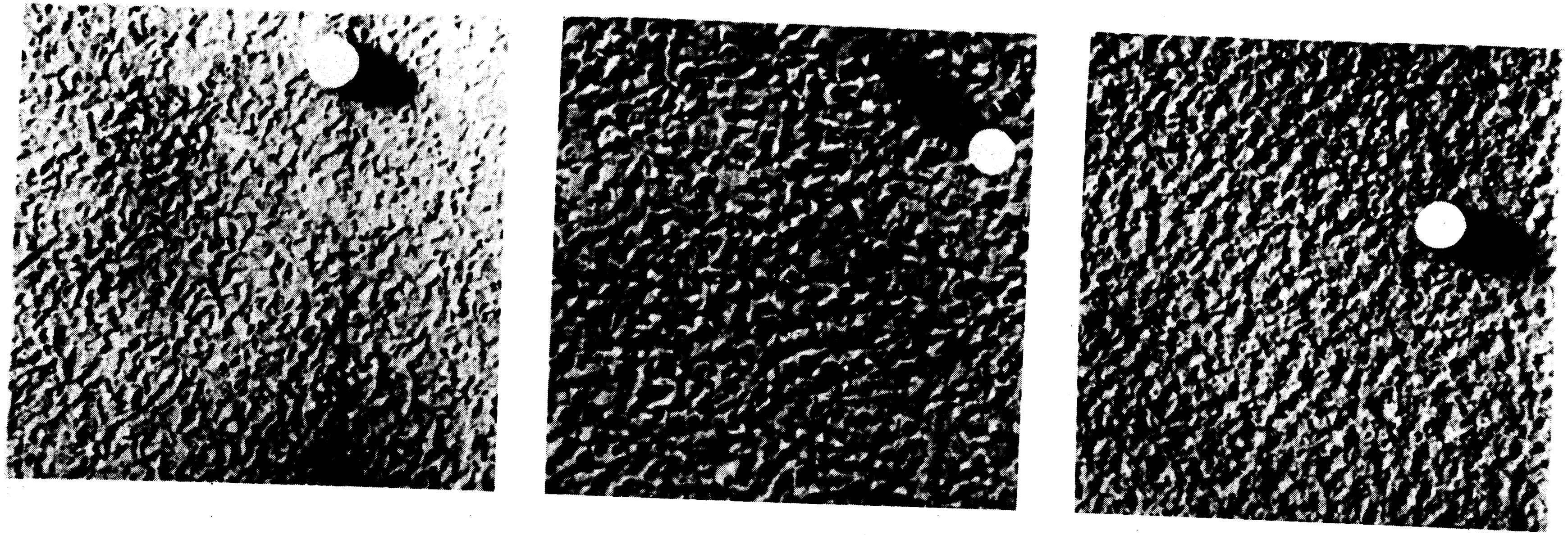
beneficial to the photoconductive sensitivity in the subsequently oxidized film.) Among the principal observations were precision measurements of the lattice parameter of PbS by X-ray back-reflection techniques. No appreciable change in spacing occurred after pre-oxidation and there had accordingly not been any extensive substitution of oxygen for sulfur or any other change in the PbS phase. Small amounts of lead sulfate ($PbSO_4$) were found in some pre-oxidized material but none of the basic sulfate phases as reported below for the oxidized films. In some experiments, small amounts of PbO were added to the PbS before evaporation, but none of these variations in the material before evaporation correlated specifically with the composition of the film after evaporation.

The process of evaporation and condensation introduces additional lines in the diffraction pattern obtained by reflection of electrons from the film. This is mainly a surface effect since it did not appear in X-ray patterns from the same films; indeed, nearly all the material in the condensed films showed the same PbS lattice spacing in the X-ray back-reflection patterns as had been observed in the material before evaporation. This was true even for material which had been heavily pre-oxidized or mixed with small amounts of PbO before evaporation. The extra lines which appear in the electron reflection patterns are not directly dependent on any particular pre-oxidation treatment. From two films extra diffraction lines were identified for a mixture of Pb and PbO (in addition to the pattern of PbS), but in most patterns the extra lines were too few and too faint to allow positive identification of the additional phases.

Of special interest was the complete disappearance of the extra lines on aging; even two minutes aging was enough at 350°C, while 30 minutes sufficed at 200°C. This suggests that the chemical aberration on the surface diffused into the PbS film since the lower temperature is too low for evaporation or dissociation of the probable phases. Since the diffusion into the film did not disturb the lattice spacing of the PbS as measured with high precision, the amount of the extra phases originally exposed to the electron beam was extremely small, or, after diffusion, it was still located on the surfaces of the crystallites although in much less concentration on the upper exposed surfaces.

2. Composition of Films Heated in Air.—The chemical compositions of the phases formed on heating lead sulfide films in air were studied as a function of the oxidizing conditions. For most of the films examined they were condensed as described at a predetermined substrate temperature and then exposed at the same temperature to oxygen or dry air at a pressure of 0.5 mm or about 740 mm for times ranging from one to thirty minutes. The physical effect of the attack of oxygen on the films is illustrated in Fig. 4; attack by air at 0.5 mm and 300°C for ten minutes has not altered the crystallites but many little grains appear on the surfaces of the crystallites (showing as pits in the replica in Fig. 4c) after attack at 1 atmosphere for 20 minutes.

Three oxidation products have been positively identified in the electron-diffraction patterns from oxidized films. The orthorhombic form of PbO in addition to PbS appears in Fig. 5a (oxygen at 0.5 mm for three minutes at 200°C). The basic sulfate, $PbO \cdot PbSO_4$, called lanarkite, is shown in Fig. 5b and another basic sulfate, $4PbO \cdot PbSO_4$, appears in 5c; the patterns shown here were obtained at different stages in the preparation of photosensitive films by the "layering" technique discussed in the next section. The identification of all three phases by comparison with standard diffraction patterns is given in the Appendix.

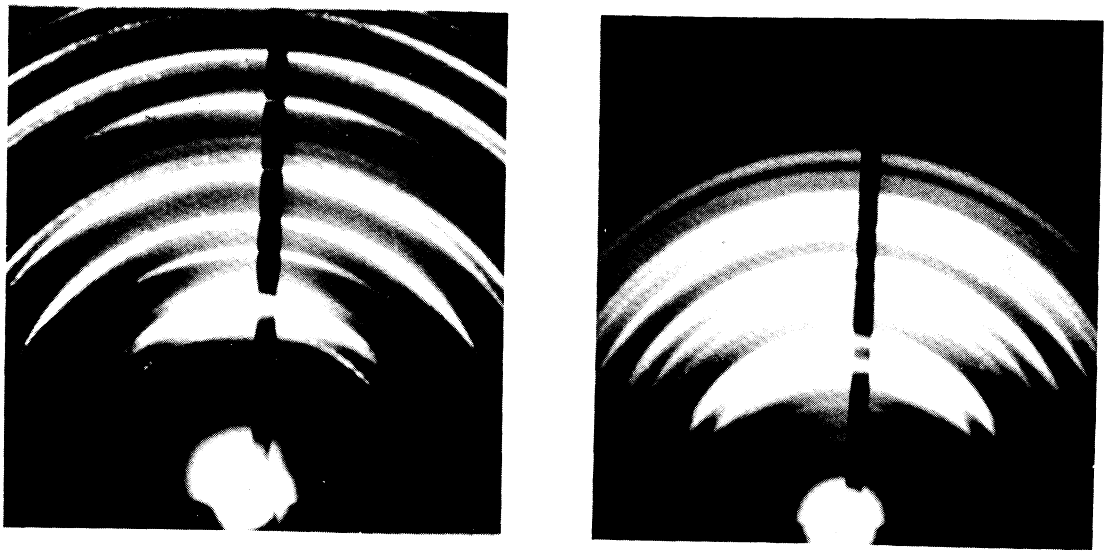


a. Unoxidized

b. Air - 0.5 mm, 10 min, 300°C

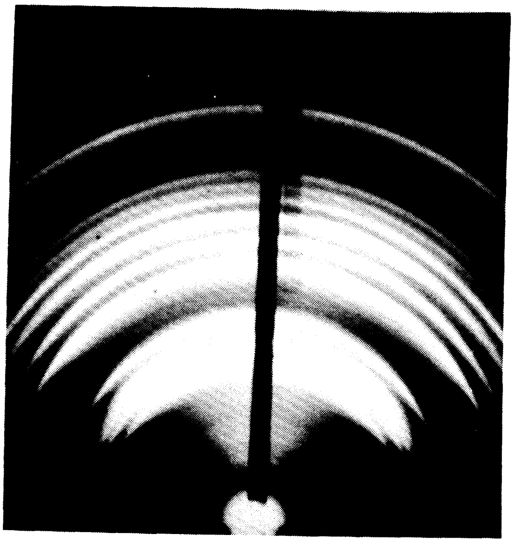
c. Air - 1 atm, 20 min, 300°C

Fig. 4. Appearance of oxidized PbS films on glass (electron micrographs—25,000X).



a. PbO + PbS

b. $PbO \cdot PbSO_4$



c. $4PbO \cdot PbSO_4$

Fig. 5. Oxidation products formed on PbS films (diffraction patterns).

It was of some interest to investigate the effect of contact with water on the condensed PbS films since chemically deposited films and those evaporated onto crystals of NaCl do come in contact with water. Figure 6 shows the pattern obtained on immersion in water for 30 minutes of a film condensed on glass at 200°C; this pattern is due to the basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$. This treatment applied to unoxidized films produces some of the basic carbonate with predominant amounts of PbS still on the surface; the oxidized films after exposure to water show only the basic carbonate.

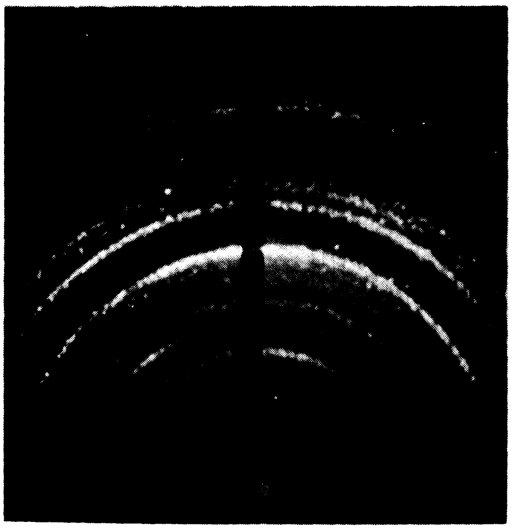


Fig. 6. PbS film showing basic lead carbonate after immersion in water (diffraction pattern).

3. Observations of Photoconductivity.—The systematic investigation of photoconductive sensitivity in films on glass made use of films prepared by the "layering" technique described in Section IV-B. In brief, the glass substrate was held at a temperature near 290°C and a succession of seven 0.15μ layers of PbS was condensed. After each condensation dry air was admitted to 0.5 mm for three minutes and then pumped out to a pressure of 5×10^{-5} mm. After the final oxidation step the air was maintained at 0.5 mm while the temperature was dropped to

room temperature or else first raised to 405°C or 465°C before cooling to room temperature. The temperature of the final oxidation was the principal variation in the treatment of the films; the only other variation was that for some series of preparations the PbS in the evaporating cup was heated in the 0.5-mm pressure of air to provide some preoxidation before evaporating. This general technique was used more than any other since it was the first one found to give reproducible results for photoconductive sensitivity.

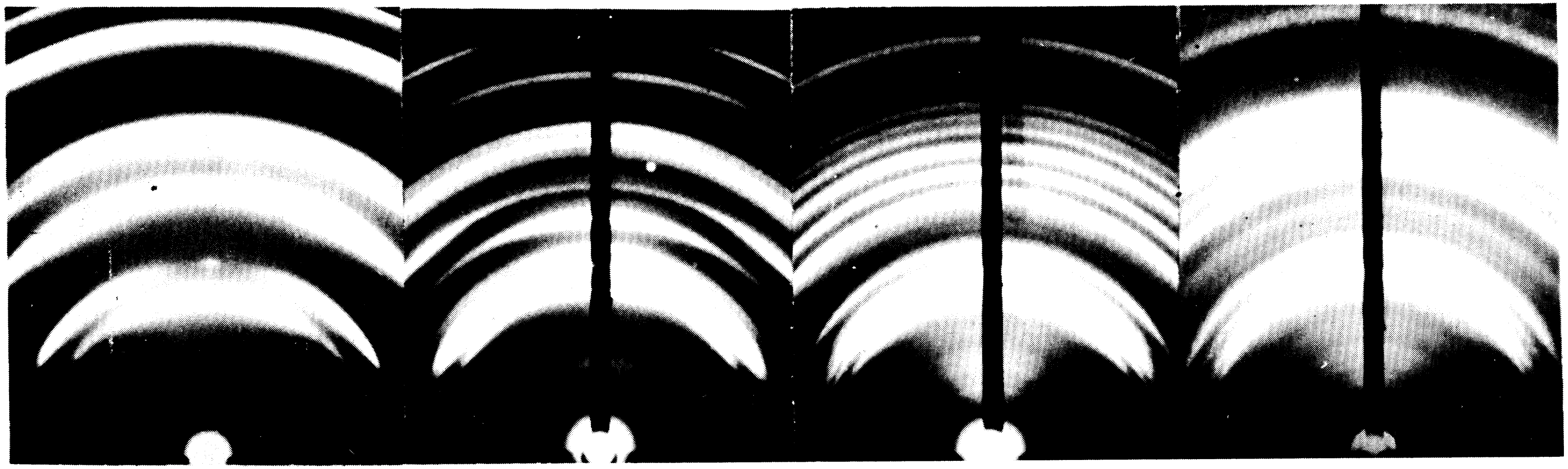
During the various steps in the preparation readings were taken of the film resistance and of the temperature. The resistance values were from 1000 to 4000 ohms after condensation and before oxidation; during oxidation, the resistance always rose by a factor of 100 or more. At the same time the temperature rose by 10° or 12°C. On pumping out the air, the temperature dropped again while the resistance remained high until the new layer of PbS was added.

For comparison of the results at different final oxidation temperatures, each of a number of films was treated in the following way. After the oxidation at 290°C, the film was cooled to room temperature and the photoconductivity was measured as described in Section IV-C with the pressure at 0.5 mm, then at 1 atmosphere of dry air, and finally after exposure to the normal room atmosphere. The film was then transferred to the electron-diffraction unit and its diffraction pattern recorded. Back in the evaporation unit the film was heated to 405°C in 0.5 mm of dry air, cooled, and its photoconductivity measured as before. Once more the electron-diffraction pattern was taken, and the film was then heated to 465°C in 0.5 mm of dry air and the photoconductivity again measured and a third diffraction pattern taken. The data on surface compositions versus photoconductive sensitivity was thus obtained for different conditions on the same film.

Figure 7 shows representative patterns for unoxidized film and for the three stages in oxidation. The patterns did not differ between films prepared with or without pre-oxidations of the PbS powder before evaporation. The patterns showed excellent reproducibility from one film to another and showed no extra lines beyond those of the identified phases. At 290°C for the final oxidation, the film surface shows PbS and the orthorhombic form of PbO; oxidation at 405°C shows some PbS along with the basic sulfate $4PbO \cdot PbSO_4$ (with occasionally a very weak PbO pattern). After 465°C oxidation, only the basic sulfate is observed.

The observed specific sensitivities (S_1) are listed in Table II for two of these series of films. The conditions of sensitivity measurements were: 15-volt d-c bias potential, 30-cm lamp to film distance, 6.0-ampere lamp current (representing a black-body temperature of about 1800°C) 200 microwatts cm^{-2} illumination on the film. All the films oxidized at 290°C showed S_1 values of about 0.01 and had PbS and PbO on the surface. After 405°C oxidation the films from pre-oxidized powder had an average sensitivity of 0.9 compared with 0.3 for the films from powder not specially pre-oxidized; both have some $4PbO \cdot PbSO_4$ on the surface. After oxidation at 465°C the corresponding average S_1 values are 15 and 2.4, and the films show only $4PbO \cdot PbSO_4$ on the surface.

The table also shows the effect of prolonged exposure to the atmosphere. The cells in the series made with pre-oxidized powder increased in sensitivity on standing for 60 days by a factor of 4- to 6-fold; the increase is less in the other series listed. Measurements made more frequently than shown in the table indicated that the cells fluctuated in intensity with changes in relative humidity, but the short time fluctuations were not more than 25 or 30%. It was also noted that some cells showed a large (as much as 10-fold) increase in specific



	a. Unoxidized PbS	b. Layered film oxidized at 290°C, PbS + PbO	c. Layered film oxidized at 405°C, PbS + 4PbO·PbSO$_4$	d. Layered film oxidized at 465°C, 4PbO·PbSO$_4$
S$_1$(I)	0	0.01	0.9	15
S$_1$(II)	0	0.01	0.3	2.4

Fig. 7. Evaporated photoconductive PbS films at successive stages in the preparation (diffraction patterns).

TABLE II

SPECIFIC SENSITIVITY AND SURFACE COMPOSITION OF PHOTOCONDUCTIVE LEAD SULFIDE FILMS IN ROOM ATMOSPHERE

Cell No.		After Oxidation at		After	After	After	After
	290°C	405°C	465°C	7 Days	20 Days	40 Days	60 Days
		Series I. Pre-oxidation of PbS Powder					
259		ABC* 2.0					
260		AC 0.87					
261	AB 0.01	ABC 0.80					
262	AB 0.01	0.70					
265	AB 0.01	AC 0.43					
266	AB 0.01	ABC 1.1	C 12	40	60	67	70
271			C 22	28	70	67	87
275	AB 0.01	AC 0.70	C 12	37	50	50	50
276			C 12	33	73	70	65
		Series II. No Pre-oxidation					
267	AB 0.02	AC 0.50	C 3.3		20	13	13
269	AB 0.02	AC 0.10	C 1.7	3.7		3.3	3.0
270			C 0.50	1.0		1.3	1.1
273-1			C 1.8	1.0	1.6	1.8	1.7
273-2			C 1.6	0.93	1.9	1.3	1.3
274	AB 0.01	AC 0.25	C 5.3	6.0	14	14	13

*Phases observed: A - PbS, B - PbO, C - $4PbO \cdot PbSO_4$.

sensitivity on the first exposure to dry air at atmospheric pressure following the low pressure (0.5 mm) used in the oxidation of the film. The effect was not general for all cells. Since the change in sensitivity required an hour or more to develop, it was possible to take electron-diffraction patterns both before and after the change; no alteration in the diffraction pattern accompanied the increase in sensitivity. Indeed the only changes in surface composition were those described above as depending on the temperature of the final oxidation, which also afforded control of the specific sensitivity over a more than 1000-fold range.

4. Other Observations.—A later re-study of the oxidizing conditions used on evaporated films of lead sulfide showed that it is possible to produce fairly high photoconductive sensitivity without the "layering" technique. This technique was devised when it appeared that surface oxidation on the particles throughout the evaporated film could not be produced by one oxidation treatment subsequent to the evaporation of a film as thick as 0.3μ. The later experiments differed from the previous ones in providing a long pre-oxidation of the lead sulfide powder (15 minutes at 500°C in air at 1 atmosphere); this pre-oxidized powder was evaporated and condensed on glass in a single 0.3-μ layer and then oxidized for 20 minutes at 290°C at 1 mm air and heated during 15 minutes to a final temperature of 465°C. The specific sensitivity, S_1, observed under the conditions listed above was 30 and the only phase appearing in the diffraction pattern of the oxidized film was again the basic sulfate, $4PbO \cdot PbSO_4$.

Some observations were made on the layered cells of the photosensitivity at elevated temperatures. For example, Cell No. 271 with S_1 equal to 22 at 24°C showed a decrease in S_1 with increasing temperature until it became less than 0.01 at 195°C, and its resistance had decreased from 900,000 to 30,000 ohms. On cooling again (still in the 10^{-4} mm vacuum), the resistance increased to 1.5 megohms and S_1 reached 1.7. A further increase to a value of 28 for S_1 was observed after one-hour contact with dry air at 1-atmosphere pressure; the resistance did not increase on exposure to air.

The electrical resistances of the cells were measured at all stages in their preparation. The resistances were always a few thousand ohms for unoxidized layers of PbS and rose to approximately one megohm on being oxidized. Increase in temperature for a film of any given state of oxidation showed a decrease in resistance, amounting to 90% or more for a 150° temperature rise in the final oxidation state. Long exposure to dry air often increased the photosensitivity but not the electrical resistance. The resistance of the cells was sensitive to exposure to atmospheric air, variations in humidity having an appreciable effect.

The noise voltages of the cells ranged from 0.3 to 3 microvolts with no correlation with the specific sensitivity. The lowest value for the noise equivalent power of all cells prepared in this study was 5×10^{-10} watts. A photovoltaic effect was exhibited by some cells as measured by interrupted illumination of the cell without bias voltage; the photovoltaic signal was no more than a thousandth of the signal from the biased cell.

Sensitivity contours were determined for one cell (No. 125) by the Naval Ordnance Laboratory, Corona. The sensitivity map (Fig. 8) has contours marked in percentages of the most sensitive region. This example shows how irregular the distribution can be. The hope of identifying oxidizing phases at the sensitivity peak led to an attempt to get electron-diffraction patterns only from the approximate area about 0.1 mm square, but it was not successful.

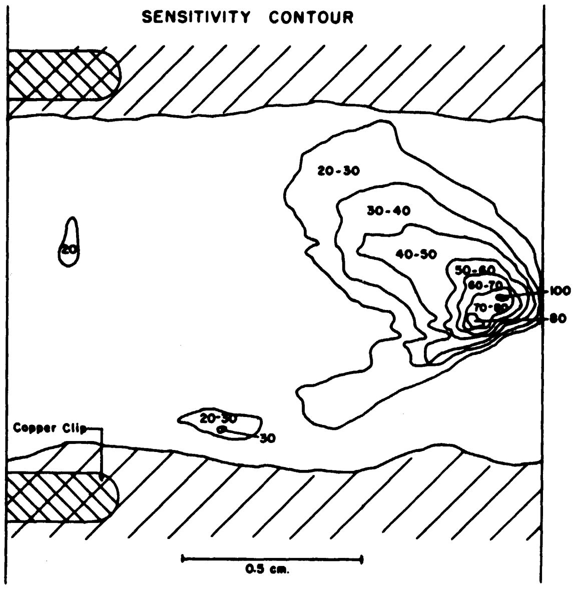


Fig. 8. Photoconductive sensitivity contour map (Cell No. 125).

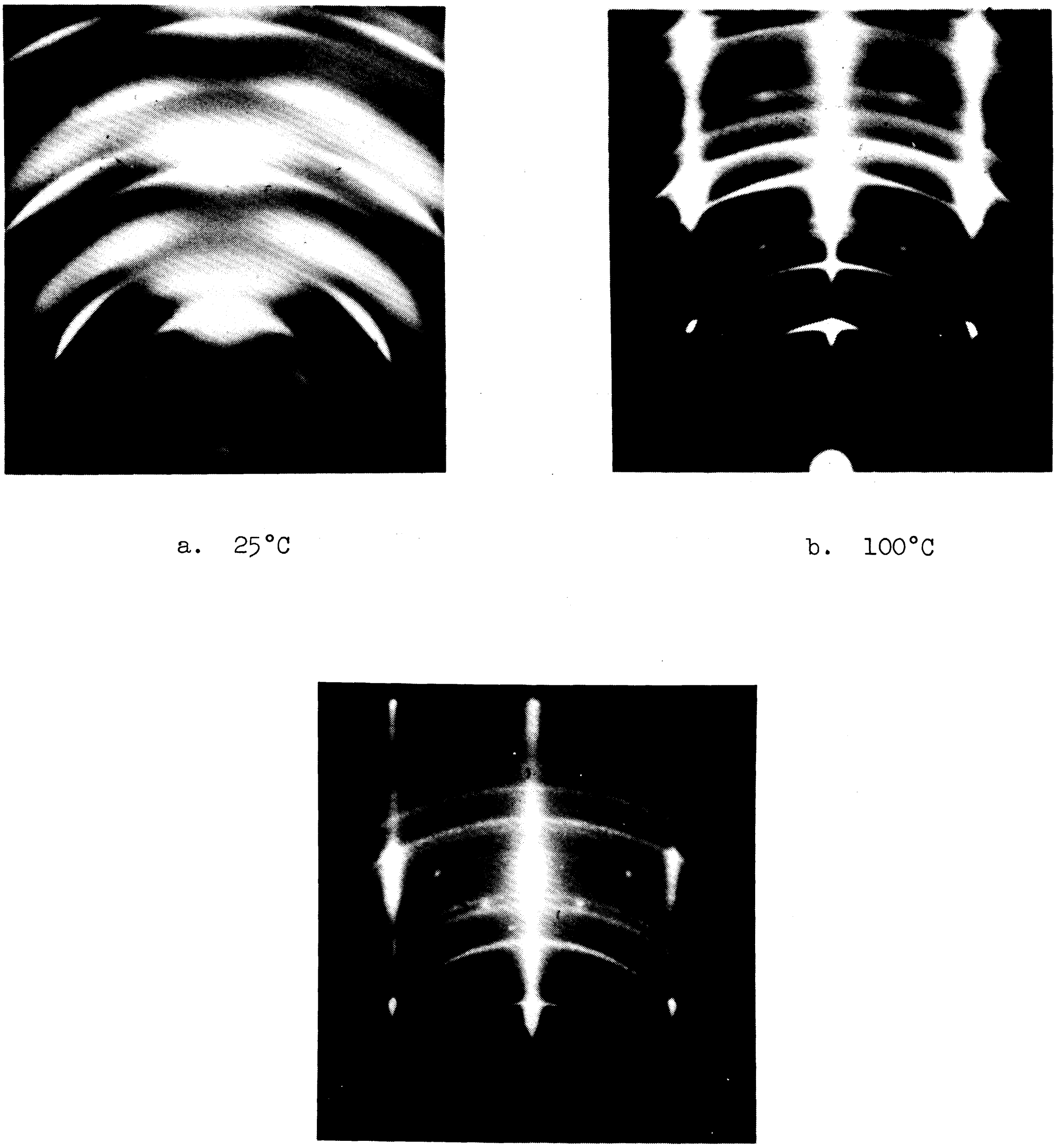
Finally a few determinations were made of the p- and n-type of the cells by a qualitative measurement of thermoelectric power. For a known temperature difference applied between the two ends of a cell, the polarity of the thermoelectric current was observed. Galena specimens of n-type were powdered and on evaporation gave n-type films. When the powdered galena was first heated with 1 mole percent of sulfur, the evaporated and condensed films were p-type; prolonged heating at 300°C and 10^{-4}-mm pressure caused a reversion to n-type. Sensitive cells prepared by the regular oxidation procedure (final heating above 400°C in 0.5-mm air) were nearly always p-type for either n- or p-type films before oxidation.

B. EVAPORATED FILMS ON SODIUM CHLORIDE CRYSTALS

1. Structure of Unoxidized Films.—Single-crystal substrates were considered for PbS films since they afforded the opportunity for giving preferred orientation and relatively large areas for various crystallographic planes in the surface of the PbS crystals. Some films were condensed on sodium chloride, mica, magnesium oxide, and diamond; but sodium chloride was used most because it afforded the most complete control of the crystallographic orientation of the condensed PbS, and it allowed the removal of the PbS film for examination by transmission diffraction and microscopy. The surfaces were prepared as described in Section IV-A.

Films of PbS condensed on NaCl at 25°C (Fig. 9a) show a higher degree of preferred orientation than on glass even at 350°C. Substrate temperatures of 100° and 200°C (Fig. 9b and 9c) give increasing order in the orientation although some random particles of PbS still show in the persistence of rings in the diffraction patterns.

At 300°C a completely oriented film of PbS is formed. The diffraction pattern (Fig. 10a) obtained by transmission through the film after dissolving away the NaCl shows that the film is a single crystal of PbS with a (100) face of the

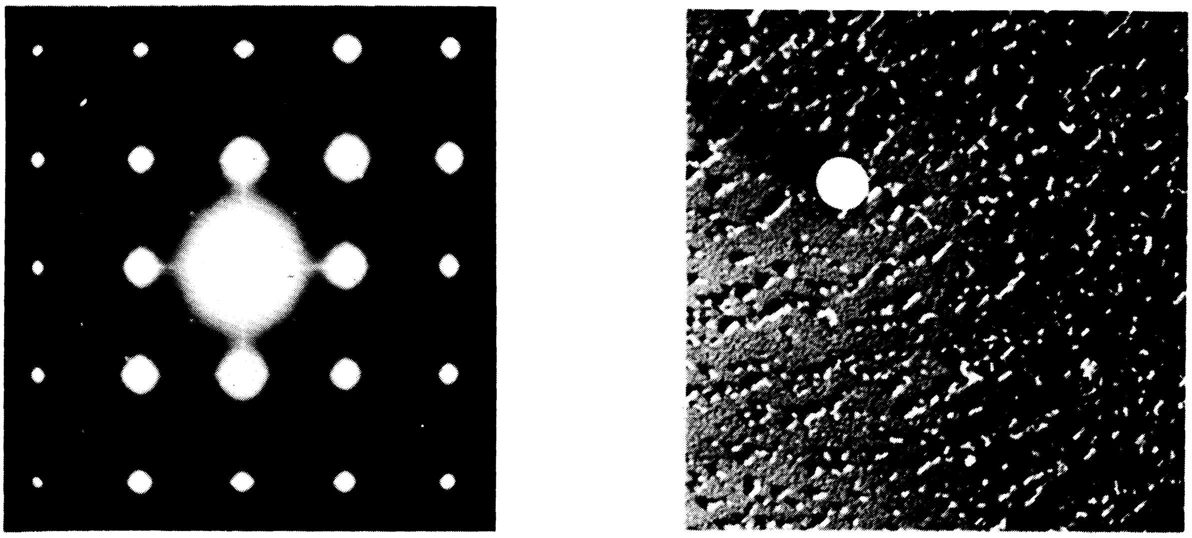


a. 25°C

b. 100°C

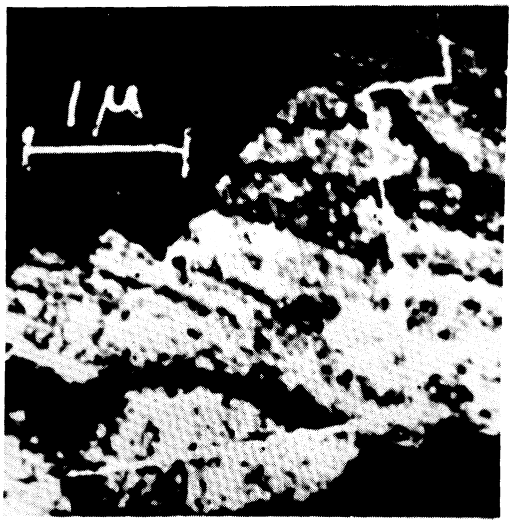
c. 200°C

Fig. 9. PbS films on NaCl (diffraction patterns).



a. Electron diffraction by transmission

b. Replica of surface (electron micrograph 25,000X)



c. Original film (electron micrograph 20,000X)

Fig. 10. PbS films on NaCl at 300°C.

cubic structure lying parallel to the surface. While each section of the film was only 3 mm in diameter after being mounted on the specimen support for the diffraction unit and microscope, the uniform orientation observed over the area of each such specimen makes it very probable that the whole 8-x-8-mm area of the film represents a monocrystalline sheet of approximately 0.2μ thickness. The replica of the surface (Fig. 10b) shows no discrete crystallites, although short surface cracks running parallel to the cubic axis directions appear. A direct micrograph is shown in Fig. 10c where cleavages parallel to the axes appear; this specimen was accidentally folded during mounting and the double thicknesses in the corners of the figure, recognized in the micrographs by their lower transmission of electrons, give rise in diffraction patterns to a variety of secondary scattering effects. The cleavages shown in Fig. 10c did not occur in specimens handled with great care and mounted on collodion film supports on the wire specimen gauzes of the microscope.

In addition to the complete (100) orientation of the PbS crystal on NaCl, other less complete orientations were observed on other single-crystal substrates with one or more zone axes of the PbS crystals normal to the substrate while having random rotations around the zone axis. For example, the <111> and <100> zones were normal to the surface in PbS condensed on freshly cleaved mica at 300°C; <100> and <110> vertical zones appeared in films on the (100) face of MgO at 200°C; only the <111> axis appeared in the vertical position in films on a natural (111) face of diamond at 200°C.

It is accordingly possible to prepare films of PbS ranging from the complete randomness of 0.1-0.3μ crystals on glass at various temperatures to the completely oriented single crystal with a (100) face on sodium chloride, including the intermediate cases of selected zone axes normal to the surface with random rotations around the zone axes. Of these various preferred orientations, only the complete one produced on NaCl at 300°C was studied in oxidation.

2. Properties of Films Heated in Air.—Oxidations were carried out on single layers of PbS on NaCl in dry air at 300°C and at pressures of 0.1, 0.2, and 2 mm, and at atmospheric pressure, for times ranging from 1 to 35 minutes. In addition, the procedure found to produce high photoconductivity in films on glass (successive layers condensed and oxidized with a final heating about 450°C) was applied to a few films condensed on NaCl.

In the oxidation of single layers, the monocrystalline nature of the PbS had a strong effect on the oxidation product. PbO crystallites produced in 35 minutes exposure to 2 mm of dry oxygen occurred with the <100> zone normal to the PbS surface; a comparable treatment of PbS on glass gave PbO crystallites in random orientation (although it is probable that each PbS crystal in the film on glass did have an orienting effect on its own cover of PbO). Predominantly single orientations of PbO on monocrystalline PbS could be produced in 15 minutes at 300°C with the oxygen partial pressure in air reduced below 0.1 mm. At air pressures of 1 atmosphere, the oxidation products showed strongly preferred (perhaps even single) orientations, but they could not be described in relation to any simple crystallographic plane.

The observations of the PbO phase formed at 300°C were made by reflection of the electron beam at glancing angles. In transmission experiments on oxidized films removed from sodium chloride, only lead sulfide was usually observed, indicating that the oxidized surface layer was never more than about 10% of the total film thickness even after prolonged oxidation. This conclusion does not necessarily apply to films oxidized on glass since the higher specific area exposed by the small crystallites should produce a proportionally greater degree of oxidation.

In transmission experiments with beam diameters of less than 200μ, occasional areas of the film were found to give patterns with diffraction rings superimposed on the array of spots due to PbS. Tilting the specimen brought new rings into the pattern. This behavior, together with the measured ring diameters, indicated the presence of the basic lead carbonate $2PbCO_3 \cdot Pb(OH)_2$, with a random rotation of crystals around a particular zone axis normal to the surface of the film. This phase is produced by the contact of the lead sulfide film with air-saturated water during the process of dissolving the sodium chloride substrate. The examination by transmission of many oxidized and unoxidized films showed that the basic carbonate is formed much more readily from the oxidized films; evidently the oxidation products react more readily with the carbon dioxide and water than the PbS itself does. This observation explains why the carbonate was the only oxidized phase observed in the transmission experiments.

Some films of PbS were applied on NaCl in successively oxidized layers with final temperatures above 450°C in order to compare the composite film with those on glass which exhibited good photosensitivity. Oxidation products on the uppermost surface gave rise to a profusion of diffraction spots but it was not possible on the limited number of films prepared in this way to make positive identification of any oxidized phase. It is not known with certainty whether the other two oxidized phases formed on the polycrystalline films (i.e., $PbO \cdot PbSO_4$ and $4PbO \cdot PbSO_4$) ever were formed on the monocrystalline films.

Measurements of the photoconductive sensitivity of oxidized films on NaCl gave values of S_1 (specific sensitivity) no higher than 0.1. The electrical resistance of these films was always lower than of those on glass; the increase in resistance on oxidation was also low. The observations suggest that condensation of a single crystal of PbS onto the NaCl substrate provided a low resistance path between the electrical contacts on the ends of the substrate. Subsequent oxidation was largely confined to the surface of the PbS crystal and did not materially affect the resistance of the body of the thin crystal. Different effects might have been observed with an arrangement of only one electrode placed on the sodium chloride covered successively by a crystalline layer of PbS, the layer of oxidation product, another layer of PbS evaporated subsequent to the oxidation, and finally the second electrode placed on top; this would provide a path between electrodes which must include the oxidized layer.

It should be noted that the experiments with PbS films on NaCl were much less extensive than on glass since the procedure for making reproducible films of good sensitivity on glass was discovered first and prosecuted with all available facilities. It still appears that a more complete study of films on sodium chloride would show the effects of different orientations of the oxidation products and of different areas of contact between the oxidized and unoxidized phases.

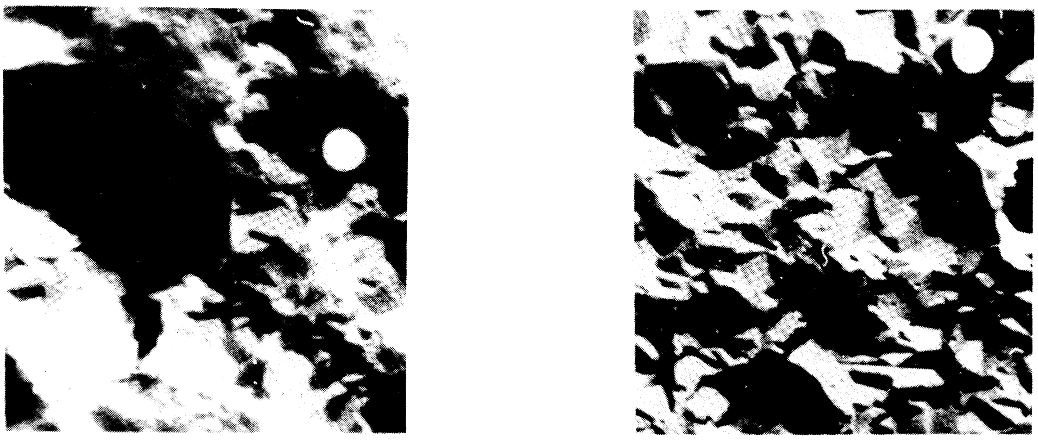
C. CHEMICALLY DEPOSITED FILMS

The examination of chemically deposited films was carried out mainly on commercial cells having known photoconductive sensitivities. While more than two hundred individual films were also prepared in this laboratory in chemical deposition experiments, it became evident that control of the many variable factors (chemical composition of the solutions; temperature, order and rate of mixing; subsequent aging and thermal treatment; etc.) to yield films of reproducible sensitivity could not be achieved without repeating the very extensive but unpublished work of the commercial laboratories. For this reason the examination of sensitive films was made on commercial cells.

Three series of cells were obtained from the Eastman Kodak Company, Rochester, having specific sensitivities (as measured under the conditions described earlier in this report) in the respective ranges of 0.05-0.1 (six specimens), 0.1-10 (six specimens), and 50-150 (three specimens). Each specimen was mounted on glass with a lead sulfide area of about 1/4 in. square between evaporated gold electrodes. No details of the preparation were available. All the specimens were examined by reflection electron diffraction and by electron microscopy of surface replicas.

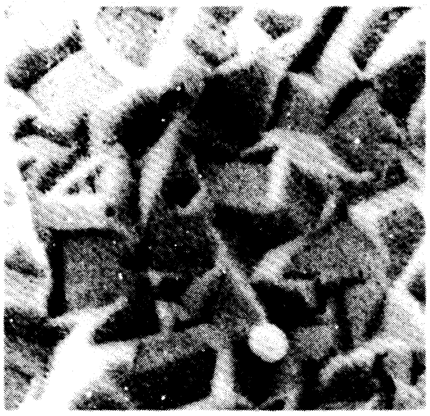
In electron-diffraction patterns, all the specimens appeared to be the same with only minor variations; these did not correlate with the different sensitivities. All films showed lead sulfide as the principal constituent together with very small amounts of the basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, showing up in some of the diffraction patterns from each of the lead sulfide cells.

The electron micrographs of surface replicas show differences which do correlate qualitatively with photosensitivity. Typical areas from one of the high-sensitivity group and one of the low-sensitivity group are shown in Figs. 11a and 11b. Both figures show well-crystallized particles of PbS ranging from about 0.05 to 0.2 micron. The high-sensitivity films show large compacted agglomerates of 2 to 3 microns in diameter. From an examination of the micrographs covering an appreciable fraction of the area of two of the high-sensitivity cells, it is evident that these agglomerates form an almost continuous framework over



a. High-sensitivity film

b. Low-sensitivity film



c. Special film

Fig. 11. Chemically precipitated PbS films (electron micrographs).

the surface. In the low-sensitivity cells, the agglomerates are much more rare and the PbS crystallites are more uniformly distributed.

Another cell with an S_1 value of 40 obtained later from the Eastman Kodak Company showed some variation from the high-sensitivity series above. In the micrograph (Fig. 11c) the PbS particles are larger (averaging 0.5 micron), show less random orientation and appear to be separated from each other by a second phase. The diffraction pattern shows only traces of basic lead carbonate accessible to the electron beam at a grazing angle to the surface.

While the very critical conditions for reproducing films of high sensitivity were not established, it was possible to make some study of the phases appearing at intermediate stages in film preparation. In the Kicinski procedure, sodium hydroxide solution is added to a solution containing lead acetate and thiourea. The first white precipitate redissolves but finally persists with the further addition of alkali and gradually darkens while a mirror-like deposit of lead sulfide forms on the walls of the container. In a typical experiment, a thin collodion substrate was used for the film support and was withdrawn from the solution when the PbS first began to appear; the transmission diffraction pattern showed randomly oriented PbS with appreciable amounts of the basic lead carbonate in a one-degree orientation (all crystals having one zone axis in common). In another experiment, the film support was removed when the white precipitate persisted but before the lead sulfide mirror had started; the only substance in the pattern was the carbonate. The carbonate was also observed in electron diffraction from the first precipitate formed when sodium hydroxide was added to lead acetate solution without thiourea; a heavy precipitate formed in this way and examined by X-ray diffraction showed the pattern of a hydrated lead oxide, $5PbO \cdot 2H_2O$. It may be concluded that in the chemical deposition the finely divided particles (such as collect on the inverted substrate for the cell) are a hydrous lead oxide which reacts with the dissolved carbon dioxide to form some of the basic carbonate, which always appears before the lead sulfide and persists in small amounts in the completed cell. There is no evidence for any relation between the amount of the residual basic carbonate and the photosensitivity of the cells.

VI. DISCUSSION

The first objective of this study was to observe the dependence of the physical and chemical composition of lead sulfide films on variations in the procedure used in their preparations. Preliminary examinations of a few photosensitive lead sulfide films showed particle sizes of 0.1μ or larger with nearly random orientation on the substrate.

The results here show that the average size and orientation of the crystallites in evaporated films can be controlled in a reproducible fashion through the choice of substrate and of its temperature during condensation. On glass a high rate of condensation (building up film thickness at 0.03μ per second) leads to particle sizes in the range from 0.01 to 0.1 micron according to the choice of substrate temperature in the range from 200° to 350°C. Larger particles (up to 0.3μ) are obtained at 350°C when a ten-times-lower condensation rate is used. The orientation is completely random at 200°; some nonrandomness appears at 350°C but is not very marked or well defined.

On single-crystal substrates, particular zones of the PbS crystallites can be obtained normal to the surface with random rotation around the normal; these zones include the <111>, <100>, and <110>. A completely oriented single-crystal film of PbS can be made to cover the whole of a sodium chloride cleavage face by condensation at 300°C; the film has the (100) plane parallel to its surface.

In chemically prepared films the particle size was observed to range from 0.1 to 0.5 micron with the smaller sizes in this range occurring more frequently than the large ones. The occurrence of agglomerates of particles (with total diameters of 2 to 3 microns) was also observed in commercially prepared test cells of high sensitivity. Sometimes the precipitated films prepared in this laboratory showed a tendency for the crystallites to have their cube faces parallel to the glass substrate, but the effect was not reproducible and did not correlate with the observed sensitivities.

The study of chemical composition shows first that under all conditions both the evaporated and the precipitated films consist mainly of lead sulfide with only traces of other phases ever present. On films heated in air or oxygen under the conditions used here, three oxidized phases have been observed: α-PbO (orthorhombic form), $PbO \cdot PbSO_4$ (lanarkite) and $4PbO \cdot PbSO_4$. In addition, $2PbCO_3 \cdot Pb(OH)_2$ is always formed when a lead sulfide film comes in contact with air-saturated water. The only other phase identified in this study was a hydrated lead oxide precipitated on the addition of alkali to a lead acetate solution and which appears to be the first solid phase formed in the preparation of chemically precipitated lead sulfide films.

The distribution of these oxidized phases is largely confined to the surface of the lead sulfide particles since electron-diffraction patterns obtained by transmission always showed lead sulfide predominantly. Even with the multiple layers oxidized between successive condensations of lead sulfide, the amount of chemical oxidation was small since the X-ray beam never showed the pattern of a second phase.

The second principal objective of this study was the observation of photoconductivity in correlation with observation on the chemical and physical compositions. This was achieved for a particular method of preparing films with reproducible properties and led to three major conclusions. (a) The specific sensitivity of the photoconductive films increases over a range of at least 2000-fold as the temperature of the final exposure to air is increased from 290°C to 465°C. (b) A change in chemical composition of the surface accompanies the increase in sensitivity. At the lowest detectable sensitivity ($S_1 = 0.01$), PbO is the only oxidized phase. With increased temperatures of oxidation and increased sensitivity, $4PbO \cdot PbSO_4$ is formed in increasing amounts until only this compound is observed on the surface of the most sensitive films. (c) The presence of a specific compound is not a sufficient condition for fixing the sensitivity since the sensitivity can be affected as much as 20-fold by a combination of mild pre-oxidation of the PbS before evaporation and of exposing the final film to the atmosphere without causing any appreciable change in the diffraction pattern of the final film surface.

The observed correlation between increased sensitivity and increased amounts of $4PbO \cdot PbSO_4$ is interesting, but it cannot be concluded that the presence of this phase causes the increased sensitivity. There are indications that a role is played by oxygen which is taken up without producing any well-characterized change in phase. For example, during the process of building up a layered photoconductive film, there are suggestive changes observed in the electrical resistance of the film. The resistance of the film increases as each freshly condensed layer of lead sulfide is exposed to air, but the increase is delayed more and more as the film thickness increases; this suggests a diffusion of oxygen occurring before the change of resistance takes place. On pumping the air away from the oxidized layer, there is little change in resistance unless the film is several layers thick; in that case the resistance drops sharply as the air is removed. Apparently much of the oxygen introduced during the later stages of the preparation is held with a very low binding energy and does not effect a chemical change in the surface but still has a marked effect on the electrical resistance. Further, the first exposure of the completed film to dry air at room temperature and one atmosphere causes a slow increase over an hour or more to a nearly steady value for the photoconductive sensitivity. Exposure to air for 20-30 days further increases the photosensitivity in some films; but none of these later treatments causes a detectable change in the electron-diffraction patterns.

Schwarz[43] has adopted the postulate that photosensitivity depends upon the presence of a chemisorbed monolayer of oxygen, which sets up intercrystalline potential barriers by trapping electrons; and he suggests that the sensitivity will be destroyed if the oxygen atoms are lost from the surface by desorption, diffusion into the lattice, or formation of oxide. The results of the present study do not fit this interpretation. The effect of heating in 0.5 mm of air at 465°C instead of 290°C is to produce more oxide and to accelerate both desorption and diffusion rather than the adsorption of oxygen; yet 1000-fold increase in specific sensitivity (as measured at room temperature) is also produced by this change in treatment.

The change observed in n-type film to p-type on oxidation which produced good photosensitivity is related to the observed effect of exposure to oxygen on the electrical conductivity. The n-type conductivity of the freshly evaporated layer of PbS is probably due to some loss of sulfur during evaporation and condensation. The first decrease in the conductivity of the layer observed on exposure to oxygen is due to the adsorption (or chemi-sorption) of oxygen atoms which trap electrons. The decrease is not reversed by reducing the gas pressure on the film. The oxygen taken up in the early stages of the oxidation treatment is not easily removed; it is held very tightly in some fashion although no new phase is detected by diffraction when the decrease in conductivity occurs on the first exposure to oxygen. Continued treatment with oxygen, particularly at temperatures near 400°C, leads to a state in the film which is now a p-type conductor, which shows (1) the presence on the surface of an oxidized phase ($4PbO \cdot PbSO_4$ on the sensitive films), (2) a reversible change in conductivity on exposure to and removal of oxygen gas, and (3) good photoconductive sensitivity. The causative relations among these different factors are not evident from the data obtained in this study, but any finally successful theory must account for the correlations observed here.

The sensitivity contours observed by the fine-spot scanning technique suggested the desirability of studying the composition of those small areas of the film showing exceptionally-high-sensitivity values. This was not achieved by electron diffraction since in reflection at the required small angles the beam path in the flat specimen is several millimeters long and in transmission the beam traversed the body of the film containing mainly PbS.

The examination of monocrystalline films made here demonstrates the feasibility of choosing the crystallographic surfaces exposed to oxidation. A more intensive study of the consequences on photoconductivity would require a technique of applying the electrodes on opposite sides of the thin film to allow only conduction paths involving the oxidized surface layer.

The results of the investigation under the conditions used show that there are definite correlations between the method of preparation of the films, their compositions, and the photoconductivity. The information on physical and chemical composition of the kind obtained here combined with an examination of other properties (e.g., spectral response) will be required for any detailed explanation of photoconductivity in oxidized lead sulfide films.

VII. APPENDIX

The identification of certain phases by comparison of the observed diffraction data with standard data for known compounds is indicated in the accompanying tables. The Bragg interplanar spacings, *d*, as measured on the diffraction patterns are compared with the values appearing in published reports on known materials or obtained in this laboratory by diffraction examination of known specimens.

Table III shows the *d* values observed on two oxidized films (Figs. 5a and b) and the standard patterns for PbS, PbO, and $PbO \cdot PbSO_4$. The letters indicate relative intensities (*s*trong, *m*edium *s*trong, *m*edium, *m*edium *w*eak, *w*eak, *v*ery *w*eak); the underlined digits in the standard patterns indicate the strongest lines in decreasing order of intensity beginning with $\underline{1}$.

Table IV shows the *d* values observed on the four films of graded photosensitivity whose patterns appear in Fig. 7. The standard patterns are for PbS, PbO, and $4PbO \cdot PbSO_4$.

Table V shows the sources in the literature of standard diffraction data for the lead-containing phases considered in this study.

TABLE III

COMPARISON OF DIFFRACTION PATTERNS OF OXIDIZED LEAD SULFIDE FILMS WITH STANDARD PATTERNS

Interplanar Spacings d (Å)				
Fig. 5		Standard Patterns		
a	b	PbS	PbO	$PbO \cdot PbSO_4$
				6.27 4
	6.15 w			6.15 4
			5.89	5.88
	5.43 vw			
	4.46 w			4.39
				4.22
				3.78
	3.69 mw			3.69 3
3.40 m	3.46 w	3.43 2		
	3.34 s			3.32 1
	3.22 vw			3.21
3.05 ms			3.07 1	
				2.99 4
2.96 ms		2.97 1		
	2.94 s		2.95 2	2.95 2
	2.83 m			2.85
2.72 m			2.74 2	2.76
				2.70
				2.62
	2.56 vw			
			2.49	2.47
	2.43 w			2.42 3
2.37 ms			2.38 3	2.40
	2.33 vw			
	2.27 m		2.28	2.27
				2.23
			2.20	
2.09 m	2.13 m	2.10 3		
	2.07 m			2.06 3
			2.01	2.03
	1.98 vw		1.96	1.97
	1.92 vw			1.91
1.84 vw	1.86 m		1.85	1.85
1.78 mw	1.79 vw	1.79 4	1.80	
1.71 w	1.73 m	1.71	1.72 4	
	1.68 m			
1.63 mw	1.62 vw		1.64	
			1.60	
	1.56 w			
1.53 vw			1.53	
			1.51	
1.47 w		1.48	1.47	
			1.41	
1.36 w		1.36	1.37	

TABLE IV

COMPARISON OF DIFFRACTION PATTERNS OF EVAPORATED PHOTOCONDUCTIVE LEAD SULFIDE FILMS WITH STANDARD PATTERNS

Interplanar Spacings d (Å)						
Fig. 7				Standard Patterns		
a	b	c	d	PbS	α-PbO	$4PbO \cdot PbSO_4$
		8.30 w	8.6 mw			8.23
		7.32 vw	7.4 w			7.38
		6.32 vw	6.4 w			6.22
	6.1 mw				5.89	
						5.78
			5.4 w			5.45
		5.25 vw				5.17
			4.2 w			4.28
			3.7 vw			
3.45 ms	3.45 mw	3.47 ms		3.43 2		
		3.23 s	3.28 s			3.24 1
	3.14 vsb		3.13 s			3.12 2
		3.07 s	3.06 s		3.07 1	3.08 3
2.96 s	2.97 vs	2.97 s		2.97 1	2.95 2	
		2.88 m	2.87 m			2.89 2
	2.73 ms				2.74 2	
		2.67 ms	2.67 ms			2.68 2
		2.60 w	2.62 w			2.59
					2.49	
		2.44 vw	2.43 vw			
	2.36 s				2.38 3	
		2.32 vw	2.31 vw			2.35
					2.28	
	2.21 vw		2.22 w		2.20	2.23
2.09 ms	2.09 mw	2.10 ms		2.10 3		
						2.06
	2.02 w				2.01	
		1.96 ms	1.98 msb		1.96	1.97 4
			1.95 msb			1.95 4
						1.87
	1.85 m	1.83 m	1.83 m		1.85	1.84
1.79 mw	1.79 ms	1.79 w	1.80 mw	1.79 4	1.80	
1.71 w	1.73 m	1.72 m	1.72 mw	1.71	1.72 4	1.73
			1.66 mw			1.66
	1.64 mw	1.64 mw			1.64	
						1.62
		1.59 mw	1.59 mw		1.60	1.60
	1.53 w				1.53	
					1.51	
1.48 w	1.47 mw			1.48	1.47	
1.36 w	1.36 w			1.36		
1.34 w	1.32 w			1.33		
1.21 w	1.21 w			1.21		

TABLE V

LIST OF REFERENCE MATERIALS CONSULTED IN IDENTIFICATION OF ELECTRON DIFFRACTION PATTERNS

Material	Literature Reference
Pb	44
PbS	45
PbO (orthogonal)	45
PbO (tetragonal)	45
Pb_2O	47
Pb_2O_3	47
Pb_3O_4	47
PbO_2	47
Pb_5O_8	48
α-PbO_x	49
β-PbO_x	49
PbO_n	48
$PbSO_3$	47
$PbSO_4$	46,50
PbS_2O_3	47
$PbO \cdot PbSO_4$	21,50
$2PbO \cdot PbSO_4$	47,51
$3PbO \cdot PbSO_4$	47
$3PbO \cdot PbSO_4 \cdot H_2O$	51
$4PbO \cdot PbSO_4$	21,51
$PbCO_3$	45
$2PbCO_3 \cdot Pb(OH)_2$	47
$5PbO \cdot 2H_2O$	52
$PbCl_2$	45
ZnO	47

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