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ELECTRON DIFFRACTION INVESTIGATION
OF
PHOTOCONDUCTIVE CRYSTALLINE LEAD SULFIDE SURFACES

QUARTERLY REPORT NO. 4

5 December, 1952, to 5 March, 1953

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Project 2037

AIR RESEARCH AND DEVELOPMENT COMMAND, U. S. AIR FORCE
CONTRACT AF 18(600)-175, E.O. NO. 355-10-2

July, 1953

enjm

UMR0548

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SUMMARY

The examination by electron diffraction and microscopy of chemically precipitated films of high and low photosensitivity has shown that both films have resolved lead sulfide crystallites of the order of 0.1-micron diameter along with some irregular agglomerates of 2 to 3 microns. The agglomerates form a nearly continuous framework in the high-sensitivity films but appear in a much lower average concentration on the surface of the low-sensitivity films. This is the first indication of a structural difference between films of different sensitivities. The characterization of the oxidized phase in these films requires the preparation of films especially mounted for transmission diffraction photographs.

Condensed films of lead sulfide about 0.15 micron thick can now be controlled in particle size between 0.01 and 0.1 micron by altering the temperature of the substrate between 200° and 350°C. Preferred orientations in the lead sulfide occur to a small degree on glass under heat treatment, and are far more pronounced on selected single crystal substrates.

No extra phase has been identified in films condensed and heated at 10^{-4} mm pressure, although extra diffraction rings appear under conditions not favoring the larger particle sizes. That they disappear on heating for three minutes at 350°C or longer at 300°C makes the formation of an oxy-sulfate on the surface of the lead sulfide an unlikely explanation of the extra rings.

Future work will include a more systematic study of the structures of chemical films, the oxidation of condensed films both on glass and single-crystal substrates, the formation of agglomerates in partially oxidized condensed films, and the testing of photoconductive sensitivity in condensed films with controlled particle size and orientation.

ELECTRON DIFFRACTION INVESTIGATION

OF

PHOTOCONDUCTIVE CRYSTALLINE LEAD SULFIDE SURFACES

STATEMENT OF PROBLEM

The use of microcrystalline lead sulfide in the preparation of sensitive photoconductive surfaces has been developed by empirical methods.^{1,2,3} Various recipes have been devised for depositing lead sulfide films on nonconducting substrates either by chemical precipitation or by condensation from the vapor followed by partial oxidation. Variations in the preparative procedures have a strong influence on the optical properties of the films. While most of the empirical information on film preparation has not been published, some reports are available^{4,5,6} on studies of photosensitivity, time of response and noise level in relation to the method of preparing the film, the frequency of the incident radiation, the temperature of the film, and the composition and pressure of the gas in contact with the film. On the other hand, knowledge of the chemical and physical composition of the films in relation to either the method of preparation or the optical properties is very meager, even though an understanding of the nature of photoconductivity certainly depends on information concerning the composition of the phases involved, the relative distribution of the phases, the effect of crystallite size and orientation in each phase, the possible variations from one crystallographic surface plane to another, and other such questions. With such information it should be possible to develop a more satisfactory control of the properties of lead sulfide surfaces and to understand something of the fundamental nature of their photoconductivity.

An investigation of surfaces to determine phase compositions and distributions as well as particle size and orientation requires electron diffraction and microscopy. The low penetrating power of electrons makes them well adapted for detecting and identifying crystalline films as thin as 30 Å when used by the reflection technique, so that it is possible to study oxidation products on a surface in the very early stage of the reaction. Collodion

replicas of the surface examined in an electron microscope contribute information on particle size, shape, and distribution. These two uses of electrons are an indispensable part of the attack on the problem of photoconductive surfaces.

Electron diffraction has been used previously^{7,8} to identify one of the possible oxidation products of lead sulfide, namely, lanarkite ($\text{PbO} \cdot \text{PbSO}_4$), but no systematic study has been reported of the oxidized phases in relation to variations in the method of preparation. The electron microscope examination⁸ of replicas of a PbS film showed particles ranging in diameter from 0.1 to 1.0 microns.

For a systematic application of electron diffraction and microscopy to the study of photosensitive films it was decided to examine such chemically prepared films as would be readily available and to concentrate at first on a more intense study of the factors affecting the structure and composition of evaporated films. The program for evaporated films includes the use of various substrates (glass and single crystals of mica, magnesia, quartz and sodium chloride) and investigations of the effect of changing the temperature of the substrate during evaporation of the lead sulfide in the range from 200°C to 400°C, the effect of different rates of condensation and different total film thickness, the effect of aging the films at various temperatures subsequent to condensation, the effect of oxidation at various oxygen pressures and temperatures, and finally the effect of exposure to normal air at atmospheric pressure. Limited tests of variation in photosensitivity with these factors are also to be made. More complete optical examinations of appropriate films will be made under the direction of Professor Brian O'Brien at the University of Rochester.

EXPERIMENTAL PROCEDURES

Electron Diffraction

The electron diffraction technique directs a well-defined monoenergetic beam of electrons onto the specimen and the pattern of diffracted electrons is recorded photographically. The pattern yields two kinds of information: (a) the identity of the crystalline phases contributing to the pattern as recognized from the Bragg d values and the relative intensities of the diffraction maxima, and (b) the occurrence of nonrandom orientation in polycrystalline specimens or recognition of the orientation of single crystals.

Lead sulfide films on glass are most readily studied by the "reflection" technique of electron diffraction in which the electron beam is directed across the film at an angle of about 1° or 2°. Because of the low penetrating

power of electrons, the resulting diffraction pattern is characteristic of an outer layer of the surface only about 30 to 50 Å thick when the surface is very smooth. On rougher surfaces, ridges as thick as about 1000 Å may be penetrated by the electrons. Since the roughness of the surface is a principal factor in determining whether all areas of the surface can be reached by the beam, the examination of surface replicas by electron microscopy is an important aid in evaluating the diffraction patterns obtained from any surface.

The transmission technique can be used on lead sulfide films which can be removed from the substrate and supported on a wire gauze. Specimens mounted in this way are turned normal to the beam so that the electrons penetrate the film in areas with thickness not exceeding their maximum range. Whenever possible, both transmission and reflection techniques are used to detect variations in composition between the surface and the bulk of the film.

The electron diffraction equipment used in this study is a standard RCA unit, Model EMD-2, purchased for this investigation. The electron beam is accelerated by 50 kilovolts and as used here has a diameter at the specimen positions of about 0.5 mm.

Electron Microscopy

The electron microscope provides information on surface contours by recording an enlarged pattern of the variations of electron transmission over a specimen consisting of a thin film. In certain phases of this study it was not feasible to remove the lead sulfide from the substrate; therefore surface replicas were used. The general field of electron microscopy, as well as the techniques of surface replication, has been discussed extensively.^{9,10} The microscope studies were made with an RCA Model EMU-2A, made available through the courtesy of Dr. T. Francis and Miss Hilda Kurtz of the University of Michigan School of Public Health.

Replicas of the lead sulfide surfaces were prepared as follows. A thin layer of a solution of collodion in amyl acetate (1:9 by volume) was flowed over the surface. On drying, the collodion film is approximately 1000 Å thick. The usual "dry stripping" method of separating the collodion with cellophane tape¹⁰ is not very successful because of the strong adhesion of the collodion to the lead sulfide. Therefore a "wet stripping" method using dilute nitric acid to loosen the collodion from the lead sulfide was developed. One end of the glass substrate is dipped into the acid in such a way that the acid reaches the edge of the collodion-lead sulfide boundary while keeping the upper surface of the collodion dry. As the lead sulfide dissolves, the collodion gradually comes free and on further slow immersion of the glass the collodion floats free on the surface of the acid. It is transferred to the surface of distilled water and allowed to soak for a few seconds. Several specimen mounts (1/8-inch-diameter wire gauzes) are then laid on top of the

collodion replica, and it is lifted from the surface of the water with a strip of wet paper (newsprint). After drying, the specimen supports and the adhering replicas are trimmed away from the remaining portions of the collodion. The mounted replica has a smooth surface next to the wire support and the detail of the lead sulfide surface is reproduced in negative on the side of the collodion away from the support.

Two further steps are used in preparing the specimens. An internal scale for calibration is provided by spherical polystyrene latex particles^{11,12} of $2580 \pm 30 \text{ \AA}$ diameter; these are deposited on the specimen from a drop of a very dilute water suspension just prior to shadowing. The replicas are shadow-cast with palladium to increase the contrast in electron transmission between different areas and to show the relief on the surface; the palladium is evaporated onto the collodion replica at an angle of 30° and the shadows of the latex particles provide a scale of distances normal to the surface and aid in distinguishing between depressions and projections on the original lead sulfide surface.

Preparation and Treatment of Specimens

The present report describes the examination of certain chemically prepared specimens supplied by the Eastman Kodak Company and of condensed lead sulfide films prepared in this laboratory. The latter have been evaporated in vacuum onto smooth glass under various condition of evaporation rate, glass temperature, and subsequent heat treatment. This has provided a study of the means of controlling the crystallite size and orientation of the lead sulfide before oxidation.

The glass substrates were 1-inch by 1/2-inch pieces cut from standard microscope slides. They were cleaned by immersing for fifteen minutes in concentrated chromic-sulfuric acid, rinsing in tap water and in hot distilled water directly from the still, and drying at 110°C in a grease-free oven. The glass pieces were handled only with clean metal tweezers. The lead sulfide used was the B and A reagent grade.

The evaporation unit was purchased from Optical Film Engineering Co., and modified by the insertion of a liquid nitrogen trap between the vacuum chamber and the high-vacuum valve.

The set-up for evaporation is shown in Figure 1. The specimen heater is a strip of 0.005-inch by 3/4-inch Nichrome sheet bent as shown; it has the advantage of low heat capacity for rapid cooling after the specimen has been condensed. The glass plate is held onto the heater by two small screw clamps, one of which also holds a thermocouple junction in position on the face of the glass. The iron-constantan junction is brazed to a thin stainless-steel plate, 3/16 inch by 7/16 inch, which is caught under the clamp to insure good thermal contact between the junction and the glass.

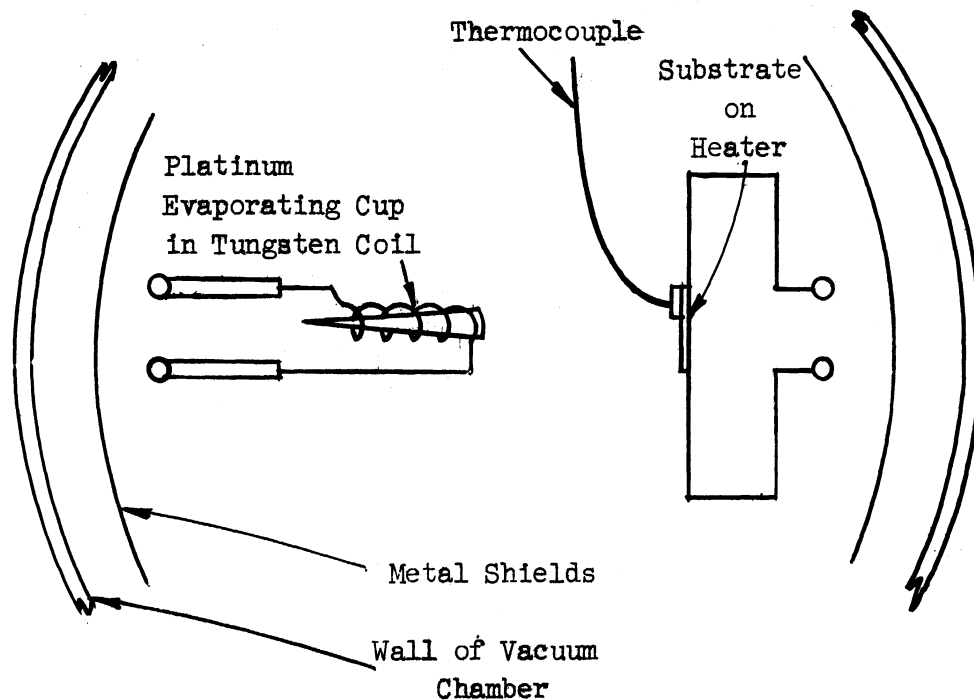


Figure 1. Top View of Vacuum Evaporation Equipment.

The procedure usually employed in preparing a lead sulfide film on glass is the following. The platinum cup is charged with a measured amount of lead sulfide powder and mounted in the tungsten filament (Figure 1), and a glass slide is mounted on the heater. The chamber is evacuated to a pressure of 10^{-4} mm Hg and the temperature of the glass raised to a predetermined value. The tungsten filament is then heated for a definite time at a definite current setting to evaporate the lead sulfide at a reproducible rate. A pressure rise for a few seconds is noted at the beginning of the evaporation, apparently due to degassing of the filament. A shiny metallic-appearing film of lead sulfide condenses on the glass. The specimen heater is turned off at the end of the condensation or later according to the heat treatment desired.

When the specimen temperature reaches about 35°C , dry air is admitted to the chamber and the specimen is transferred quickly to the electron diffraction unit. The four minute exposure to air before the vacuum is restored over the specimen in the diffraction unit probably has very little oxidizing effect on the specimen at room temperature; nonetheless the patterns are always examined for evidence of such oxidation. An effect of this air exposure on the particle size or orientation was not expected.

In the diffraction camera, the nonconducting substrate of the lead sulfide film allows some accumulation of charge from the electron beam which

must be neutralized by an electron spray from an auxiliary gun. Because of possible thermal effects on the surface from the auxiliary spray, the diffraction exposures are made in as short a time as possible.

The collodion replicas are usually prepared from the specimen upon removal from the diffraction unit.

RESULTS

Chemically Precipitated Films

Three series of chemically precipitated lead sulfide films of known photoconductive sensitivity were prepared and supplied by Dr. Hammar at Eastman Kodak Co., Rochester, New York. Each piece was approximately 1/4 inch by 3/4 inch with a 1/8-inch-wide band of gold evaporated on each end for making electrical contact with the film. Neither the method of preparation nor any subsequent treatments of the surfaces were specified.

Series A contained six pieces showing gradations in photosensitivity; Series B contained three pieces, all of very high sensitivity; Series C contained six pieces of low sensitivity.

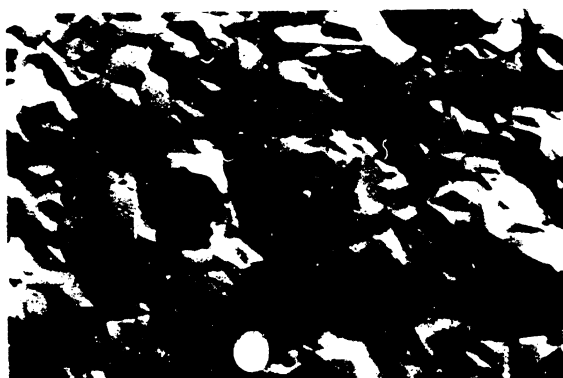
Electron diffraction patterns were obtained by reflection from all of the pieces; the same pattern with only minor variations was obtained from all (Figure 2c). The continuous rings correspond to lead sulfide, the slightly grainy character of the rings indicating a nearly random orientation of the crystallites.

The appearance of a second phase is suggested by a few diffraction spots showing in Figure 2c as bright specks between the positions of the lead sulfide diffraction rings. These specks are far too few in number to allow an identification. While the presence of an oxidized phase is presumed to be required for photosensitivity, the films as supplied do not show appreciable amounts of a second phase lying on the surface in positions that can be reached by the electron beam in the reflection technique. An attempt to strip the film from the glass for a transmission experiment was not successful.

The electron micrographs taken from collodion surface replicas do show differences correlating with photosensitivity. The dry-stripping technique was not completely successful here, so that replicas could be obtained from only two specimens in each series. A typical micrograph from Series B is shown in Figure 2a and from Series C in Figure 2b. The white circle in each of these figures is a latex ball of 0.258-micron diameter. Both figures show well crystallized particles ranging from about 0.05 to 0.2 micron. In



a. High Sensitivity



b. Low Sensitivity



c. Typical Electron Diffraction
Pattern



d. Special Film of High Sensitivity

Figure 2. Electron Micrographs (20,000 X) and Electron Diffraction Patterns of Chemically Prepared Photoconductive Lead Sulfide Films.

the high-sensitivity films large, well compacted agglomerates appear, reaching 2.0 or 3.0 microns in size (as shown in Figure 2a to the upper right of the center). From the study of the available micrographs it appears that these agglomerates are distributed over the surface forming an almost continuous framework. The low-sensitivity films in Series C show a much lower average concentration of these agglomerates and have a much more nearly uniform distribution of the small crystallites.

Both series show that the surfaces are rough, with high and low spots differing by several tenths of a micron. If any second phase occurring in the high spots has been removed by accidental rubbing of the surface, the failure of the diffraction pattern by the reflection technique to show the second phase is understandable.

Figure 2d is included to emphasize the fact that variations occur among sensitive films. This specimen was prepared by chemical precipitation at a different time from the three series mentioned above and while it was reported to have a good photosensitivity, it differs in three respects from the Series B: (a) the individual crystallites are larger (averaging nearly 0.5 micron), (b) the crystallites appear to be separated by a different phase showing nearly white in the figure, and (c) a high degree of preferred orientation of the crystallites is indicated by the diffraction patterns.

Condensed Films

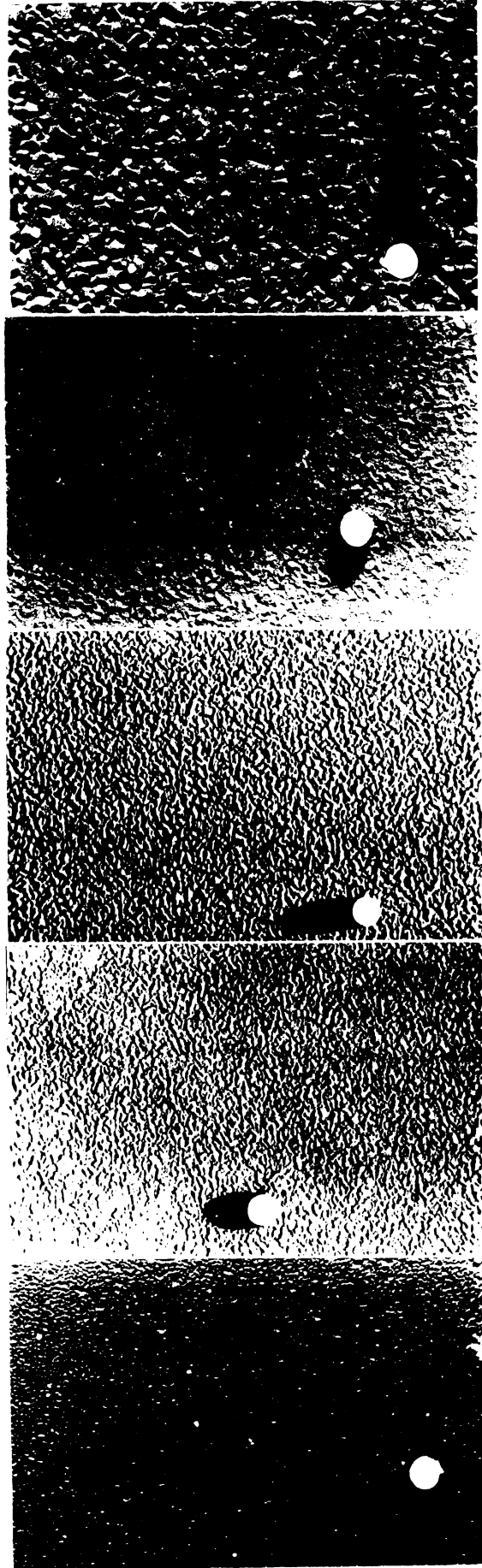
The work to date includes the examination of lead sulfide films condensed on glass at temperatures of 25°C and 200° to 350°C followed in some cases by subsequent heating at 300° to 350°C, as well as preliminary experiments using as substrates single crystals of mica, diamond, magnesia and spinel.

The films on glass were prepared by subliming 4.5 mg of reagent-grade lead sulfide powder during a three-minute period. The average film thickness is estimated at 0.15 micron from direct weighing on a microbalance. The films required twenty to thirty minutes to cool in the vacuum of the evaporation chamber. The results are summarized in Table I, and Figure 3 and 4 show micrographs and diffraction patterns.

The principal observation from the micrographs in Figure 3 is that the film shows a graininess of dimensions of about 0.01 micron but no distinct crystal faces at 200°C, with a gradual change to clearly defined crystals of about 0.1 micron size at 350°C. Higher temperatures might lead to still larger crystal sizes, but the present experiments in vacuum (i.e., residual pressure of 10^{-4} mm) lead to re-evaporation of the film at higher temperatures.

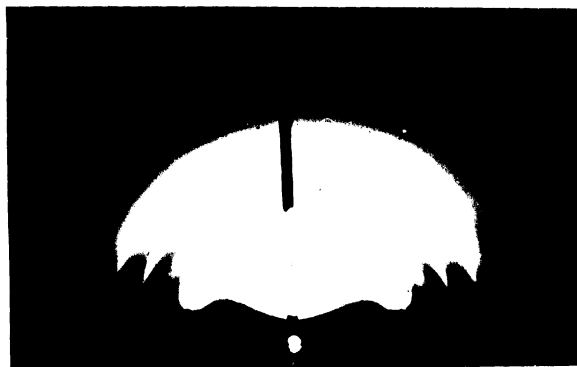
TABLE I
 CHARACTERISTICS OF LEAD SULFIDE FILMS
 EVAPORATED ON GLASS SUBSTRATES

Substrate Temperatures	Nature of Diffraction Pattern	Nature of Electron Micrograph	Figures
200°C	Somewhat blurred. Fairly intense extra rings.	Uniform, grainy. No definite crystal faces at 20,000X.	3a, 4a
225°	Little change	Little change	
250°	Sharper PbS rings. Same extra rings	Coarser. Still no crystal faces.	3b
275°	Similar to 250° Extra rings slightly fainter.	Still coarser than 250°.	3c, 4b
300°	Relative intensities of rings different. Pre- ferred orientation of PbS. Extra rings much fainter.	Crystal faces begin to appear.	3d
325°	More orientation. Extra rings much fainter.	Crystals about 0.05 micron.	4c
350°	More orientation. Practically no extra rings.	Crystals up to 0.1 micron.	3e, 4d



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

Figure 3. Electron Micrographs of Lead Sulfide Films Condensed in Vacuo on Glass at Various Temperatures (20,000X)



a. 200°C



b. 275°C



c. 325°C



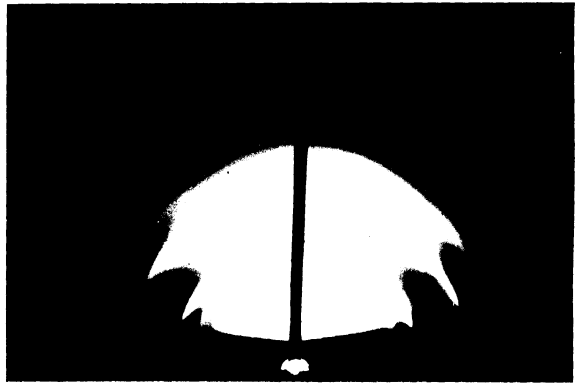
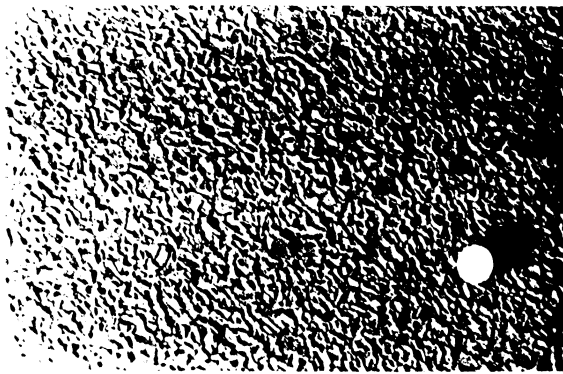
d. 350°C

Figure 4. Electron Diffraction Patterns of Lead Sulfide Films Condensed in Vacuo on Glass at Various Temperatures.

The electron diffraction patterns also show the effect of increasing crystallite size, as indicated by increased sharpness of lead sulfide diffraction lines, as well as the tendency with increasing temperature toward orientation of some crystallites relative to the glass surface. The diffraction patterns show rings in addition to those of lead sulfide at the lower temperatures but not at temperatures near 350°C . Although four or five of these "extra" rings could be measured in many of the patterns, it has not yet been possible to match them satisfactorily with any compound which might conceivably be formed and for which comparison patterns are available.

Additional experiments were carried out on the effect of heating subsequent to condensation and of a more rapid condensation rate. Figure 5a shows the micrograph and diffraction pattern for a film condensed at 300°C and heated for two hours at the same temperature. The faint extra rings apparent at the end of the condensation (Figures 4b and 4c) have almost entirely disappeared here, while the heating has increased the particle size and has produced some preferred orientation of the lead sulfide with the (111) plane parallel to the glass. Another film heated to 350°C for one hour shows similar effects (Figure 5e) with particle sizes now in excess of 0.1 micron and some orientation of the (100) plane parallel to the glass. The diffraction pattern in Figure 5b shows the effect of condensation of the same amount of lead sulfide in one minute instead of the usual three minutes, followed by immediate cooling. In comparison with Figure 4d it is observed that the one-minute condensation leaves intense extra rings similar to those produced at lower temperatures, whereas none appear in the three-minute condensation.

Preliminary experiments have been started to study the effect of a more pronounced preferred orientation of the lead sulfide. This is achieved by using single-crystal substrates in place of glass. Different substrates should lead to different crystallographic planes appearing on the surface of the lead sulfide film with possible variations in photosensitivity following partial oxidation. The crystal faces used as substrates include: the cleavage face of mica, the (111) and (110) faces of diamond, the cleavage (100) face of magnesia, and the (100) face of spinel (magnesium aluminate). The diffraction patterns from lead sulfide condensed on three of these are illustrated in Figure 6. A strong preference for the (100) plane of lead sulfide parallel to the surface is shown in Figure 6b and for (111) in Figure 6c. In each case there is random orientation around the normal to the plane. Consideration of the strong orienting effect of these substrates suggests the use of sodium chloride, whose structure is the same as that of lead sulfide and whose interionic spacings are nearly the same. In general it is found that the greater the similarity between substrate and overgrowth, the stronger the tendency for preferred orientation.



a. 300°C - Heated 2 hr in Vacuo

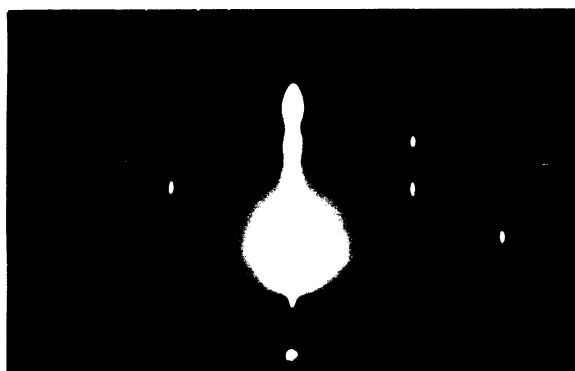


b. 350°C - Higher Evaporation Rate



c. 350°C - Heated 1 hr in Vacuo

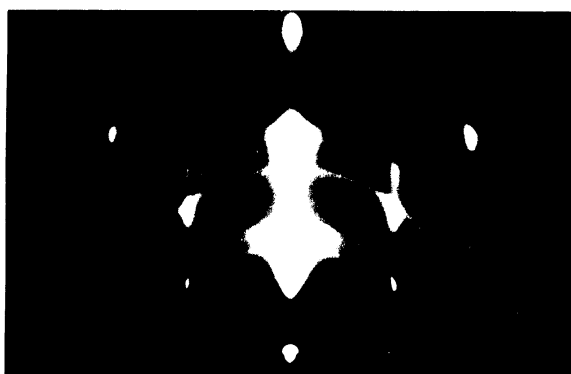
Figure 5. Electron Micrographs (20,000X) and Electron Diffraction Patterns of Lead Sulfide Films Condensed on Glass under Various Conditions.



a. On Cleaved Mica - 300°C



b. On Cleaved MgO - 200°C



c. On (111) Diamond Face - 200°C

Figure 6. Electron Diffraction Patterns of Lead Sulfide Films Condensed on Monocrystalline Substrates.

DISCUSSION

The chemically prepared films in Series B and C have led to the first indication of any consistent difference in physical structure between lead sulfide films of high and low photosensitivity. A systematic study of chemical films would show whether the particular structure observed in Series B films is essential to very high sensitivity in chemical films. The question of the nature and distribution of the oxidized phase can be followed by three different experiments: (a) the examination of chemical films carefully protected to avoid the accidental removal of any material from the surface of the film, (b) the mounting of chemical films on a thin continuous support such as collodion to allow transmission diffraction patterns for the detection of second phases in the body of the lead sulfide film, and (c) the examination by diffraction of very thin deposits of lead sulfide from aqueous solution onto a wire gauze in an attempt to study separate particles of the chemical precipitate before agglomeration. A thorough study of chemical films will be undertaken, as additional personnel becomes available, because of the interesting contrasts between the chemically precipitated and the evaporated films. One example of this difference is the great decrease in photosensitivity on exposure to air, shown by evaporated films but not by those precipitated from solution.

The experiments on evaporated films have prescribed the conditions for controlling the particle size of the lead sulfide crystals between about 0.01 and 0.1 micron. The results on the Series B chemical films suggest an attempt to produce agglomerates of the 0.1 micron condensed particles either during or following a partial oxidation. This agglomeration might be accomplished by heating to temperatures of 500°C, in which case an appreciable pressure of an inert gas will probably have to be present in the evaporation chamber to suppress the evaporation of the lead sulfide. Extended heating of the condensed films without oxidation apparently leads only to an increase in the size of the individual crystals; an increase beyond the 0.1-micron size without providing a coating of an oxidized phase is probably not desirable. This suggests that the extended heating should be done with some residual pressure of oxygen.

The occurrence of extra rings in the diffraction patterns from specimens condensed at 10^{-4} mm pressure raises the question of oxidation even at this pressure (although the extra-ring pattern has not yet been identified). Another possibility is a deficiency structure accompanying a deviation from the stoichiometric ratio between lead and sulfur as the result of the process of evaporation and condensation. In either case, the interesting dependence of these rings on the temperature and rate of condensation and subsequent heating must be explained. It may be, for example, that the higher temperature for a longer time preferentially favors the migration and crystal growth

of the lead sulfide with a covering up of the second phase. The answer to this suggestion depends on obtaining transmission diffraction patterns through the heat-treated films.

In addition to a better characterization of the lead sulfide films evaporated onto glass, further work will include studies of films on sodium chloride and of the oxidation of films, both on glass and sodium chloride, to produce a detectable photosensitivity. It is noted that the photosensitivity will have to be tested on films while mounted in the evaporation chamber to avoid the loss associated with exposure to the atmosphere. The chemical effect of the exposure to air is a subject for later study.

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