RADIO CORPORATION OF AMERICA

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FINAL REPORT

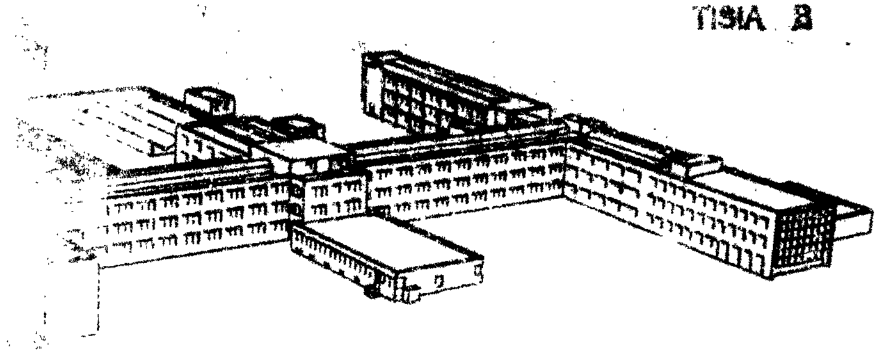
RESEARCH STUDY FOR
INCREASING THE SENSITIVITY OF PHOTOEMITTERS

(UNCLASSIFIED TITLE)

CONTRACT DA44-009-ENG-4913

29 DECEMBER 1961 - 31 MARCH 1965

CONVERSION DEVICES LABORATORY
ELECTRONIC COMPONENTS AND DEVICES



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RESEARCH STUDY FOR
INCREASING THE SENSITIVITY OF PHOTOEMITTERS

Contract No. Da44-009 ENG-4913

FINAL REPORT

for the period
29 December 1961 - 31 March 1965

for

U.S. Army, Corps of Engineers
ENGINEER RESEARCH AND DEVELOPMENT LABORATORIES
Ft. Belvoir, Va.

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FIGURE CAPTIONS

PURPOSE

To investigate the physical and structural properties of photoemitting materials, to study and develop processing procedures for producing improved photocathodes, and to investigate the possibilities of field induced photoemitters.

ABSTRACT

A summary of the work performed during this contract is presented. This includes a study of variations in processing and composition of S-20 cathodes and the investigation of antimony films deposited from Sb and PtSb beads. Two different phases of K_3Sb are described. Formation of photocathodes by sequential and simultaneous deposition from molecular beams of the constituents has been examined. The crystal structure of alkali antimonides and other photocathode systems has been studied by means of x-ray and electron diffraction. Attempts to produce shallow p-n junctions in germanium for field induced photoemission are described.

I. INTRODUCTION

The work done under this contract was directed primarily towards gaining a more complete understanding of the S-20 photocathode with the ultimate goal of improving both its response and the processing techniques for fabricating this cathode. In addition, part of the effort under this contract was directed towards attempting to develop a field induced photoemitter which would be sensitive to infrared radiation.

The results of these investigations will be reported under the following headings:

(1) Study of S-20 cathode parameters including variations in processing, composition, and study of the components which make up the S-20 system.

(2) Formation of photocathodes by use of molecular beam techniques including the development of the molecular beam techniques and the preparation of photocathodes by sequential and simultaneous deposition.

(3) Study of photocathodes with emphasis on the alkali antimonide system by use of x-ray and electron diffraction techniques.

(4) Attempts to produce and study shallow p-n junctions in germanium for use as field induced photoemitters.

II. STUDY OF THE S-20 PHOTOCATHODE PARAMETERS

In the course of this contract a large number of experiments were performed involving modifications of the standard activation process of S-20 cathodes as well as modifications of the cathode composition. Since the details of these experiments have been described in Quarterly Reports this Final Report will represent a brief summary of the results but ample references to the Quarterly Reports (in Roman numerals) will be given for the reader who is interested in the details.

In order to make the purpose of the experiments covered by this report clearer, a brief description of the "standard" activation procedure for S-20 cathodes (II, p.3) will be given first. The initial step of the process consists of evaporating a thin film of Sb, whose thickness is determined by its light transmission. This Sb film is then exposed to K-vapor at 160°C to form K_3Sb. Next, the K is partially replaced by Na by exposing the K_3Sb cathode to Na-vapor at 220°C until a compound of the composition $Na_{>2}K_{<1}Sb$ is obtained. As a fourth step, K and Sb are added in alternation at 160°C to produce the stoichiometric compound Na_2KSb. Finally, Cs and Sb are introduced in alternation to obtain the S-20 cathode.

This process has many undesirable features, such as:

1. It is time consuming and requires skilled operators.
2. The thickness of the cathode is not reproducible because even with identical thickness of the Sb base layer, the amounts of Sb and alkali metal added in later stages of the process are irreproducible.
3. The necessity of changing the processing temperature at least twice during the cathode formation leads to undesirable temperature gradients between tube envelope and internal electrodes.
4. Whereas the sensitivity to white light, expressed in microamperes

per lumen, can be reproduced within acceptable limits, the long wavelength response above 7500 A varies from tube to tube by orders of magnitude without known changes in the processing. In other words, the essential parameter(s) for long wavelength response are not yet known.

All of the experiments described below were motivated by these problems, i.e., the goals were essentially twofold: to improve and simplify the process and to understand the relationship between processing parameters and photoelectric characteristics, with special emphasis on long wavelength response.

A. Processing Modifications

The number of processing parameters in the S-20 process is so large and they are frequently so interdependent that it is difficult to separate clearly the effect of any single parameter. The most important modifications investigated under this contract were concerned with the following parameters:

1. Thickness of initial Sb film.
2. Sequence of introducing alkali metals.
3. Changes in processing temperature.

Although these three parameters overlapped in many experiments an attempt will be made to discuss the results under these three headings.

1. Thickness of Initial Sb-Film

As was pointed out above, the initial Sb film does not uniquely define the thickness of the final S-20 cathode because of subsequent additions of Sb during the process. However, the final thickness obviously depends largely on the initial thickness. In semi-transparent photocathodes the thickness is critical inasmuch as the escape probability of photoelectrons is reduced if the light is absorbed too far from the vacuum interface, i.e., if the cathode film is too thick; on the other hand, the efficiency of the cathode is reduced if the film is so thin that a substantial fraction of the incident light is not absorbed. From light absorption curves (see W.E. Spicer, Phys. Rev. 112, 114 (1958)) of S-20 cathodes it is known that the absorption in the visible spectrum decreases rapidly from short to longer wavelengths. It follows that for the S-20 cathode the optimum thickness for high photoemission will increase with wavelength.

Because of the importance of extending the response of S-20 cathodes to longer wavelengths attempts were therefore made to improve the long wavelength response at the expense of blue response by making the cathodes thicker. The results indicated (VII, p.11) that the near infrared response can, in fact, be increased in this way but by not more than a factor of two. If the thickness is further increased the reduced escape probability of the electrons apparently more than compensates for the increased light absorption. Moreover, the greater thickness does not substantially affect the threshold wavelength. Thus the conclusion from these experiments is that the quantum efficiency in the red and near infrared can be, at best, doubled at the expense of blue response, but that the thickness does not appreciably influence the long wavelength threshold. For all applications where short wavelength response is not required and high efficiency to red light is essential, the improvement obtainable with thicker Sb base layers seems worthwhile. For instance, an initial Sb film corresponding to 40% light transmission seems to be preferable to one of 70% light transmission (VII, Table III).

2. Sequence of Introducing Alkali Metals

If the standard process is represented by the symbols Sb-K-Na-(Sb + K)-(Sb + Cs) (where the + sign indicates alternation of the elements), a first series of investigated modifications can be summarized as follows. (Unless indicated otherwise, K and Cs are introduced at 160°C and Na at 220°C).

(a) Sb-K-Cs-Na - (Sb + K) (VI, p.8)

(b) Sb-K-Cs - (Sb + Na at 160°C) (X, p.3, VI, p.9)

(c) Sb-Na-Cs (at 220°C) - (Sb + K) (VII, p.16)

(d) Sb-K- (Sb + Na at 180°C) - (Sb + Cs) (VI, p.8)

These processing changes produced sensitivities equal or inferior to those obtained by the standard method and did not show any advantages with regard to reproducibility or simplicity of activation.

In a second series of modifications the aim was to eliminate the need for adding Sb beyond that evaporated as initial base layer. Most of these experiments were based on the observation (VIII, p.2ff) that at 220°C K can replace Na in the alkali antimonide compound although the vapor pressure of K is higher than that of Na. This should make it possible to convert Na_3Sb or $Na_{>2}K_{<1}Sb$ into Na_2KSb without subsequent alternation of Sb and K. The following sequences were tried:

(a) Sb-K-Cs-Na (X, p.5)

(b) Sb-Na-K at 220°C - Cs (VIII, p.4ff, IX, p.3)

(c) Sb-Cs-Na-K at 220°C (IX, p.4)

(d) Sb-K-Na-K at 220°C - Cs (IX, p.4)

(e) Sb-K-Cs-Na-K at 220°C (IX, p.5)

These experiments produced two results. First, it proved possible to obtain Na_2KSb (S-24) cathodes of normal sensitivity by replacing Na with K at 220°C without the need for additional Sb evaporation. Second, in all cases additional Sb was needed in alternation with Cs to obtain optimum S-20 response. Thus this type of process is advantageous for making S-24 cathodes with single Sb evaporation, but it is of no practical value for the S-20 cathode until a successful method of introducing the Cs in a single operation has been found.

3. Changes in Processing Temperature

Based on the observation that Sb reacts with Na at temperatures as low as 160°C, a series of experiments was made with the aim of using a constant temperature of 160°C during the whole formation process. The following sequences were tried:

(a) Sb-Na at 160°C - (Sb + K) - (Sb + Cs) (X, p.3)

(b) Sb-K-Cs- (Na + Sb at 160°C) (X, p.3)

(c) Sb-K- (Sb + Na at 160°C) - (Sb + Cs) (X, p.4)

Method (c) proved unsuccessful. Methods (a) and (b) produced normal Na_2KSb cathodes but the final S-20 cathode was in all cases low in red response. Since the red response could be improved by subsequent processing at 220°C one is forced to the conclusion that the temperature at which Na is introduced affects the sensitivity only after adding Cs and not, as one would expect, the formation of Na_2KSb.

B. Study of New Cathode Compositions

The new cathode compositions studied under this contract can be considered under three headings, viz., the Sb-K-Cs cathode, cathodes containing oxygen, and miscellaneous new combinations.

1. The Sb-K-Cs Cathode

During experiments with S-20 cathode processing, the observation was made that after the introduction of K and Cs, but before the addition of Na, higher sensitivity can be obtained than with either of the mono-alkali antimonides, K_3Sb or Cs_3Sb. Therefore a systematic investigation of the combination Sb-K-Cs was undertaken (V, p.13ff, VI, p.9ff). This work led to a well defined material of the stoichiometric formula K_2CsSb.

The following are the most important characteristics of the K_2CsSb photocathode (see also A.H. Sommer, Appl. Phys. Letters 3, 62(1963), W.H. McCarroll, J. Phys. Chem. Solids 26, 191(1965)). The photoelectric response is distinguished by exceptionally high quantum efficiency below 4500 A. An average curve is shown in Fig. 1, but quantum efficiencies in the region of 40% at 4000 A are not uncommon. The response drops sharply toward longer wavelengths and the red response is negligible. The cathode has lower thermionic emission at room temperature than any other cathode with high sensitivity to visible light and dark currents as low as $2x10^{-18}$ amps/cm^2 have been obtained. An undesirable feature of the cathode is its high resistivity at room temperature which limits the photocurrents to very low values unless a conducting substrate (see below) is used.

To extend the usefulness of the K_2CsSb cathode, two improvements would be desirable, viz., greater conductivity and increased red response. The conductivity problem was solved satisfactorily by using a substrate of evaporated chromium. It was found (VI, p.10) that sufficient conductivity is obtained with a Cr film which transmits 85% of the incident light and that through improved optical coupling the actual light loss may be less than 15%. With this substrate the cathode becomes useful in image tubes where only blue response is required, for instance in the second stage of intensifier orthicons or of multi-stage image tubes where high response to a blue phosphor is required.

Attempts to improve the red response have only been partially successful. It was found that the red response can be considerably improved (V, p.13, VI, p.13) by superficial oxidation, but the highest sensitivity thus obtained is still inferior to that of an average S-20 cathode.

2. Cathodes Containing Oxygen

In all photocathodes with high sensitivity to visible light (S-1, S-10,

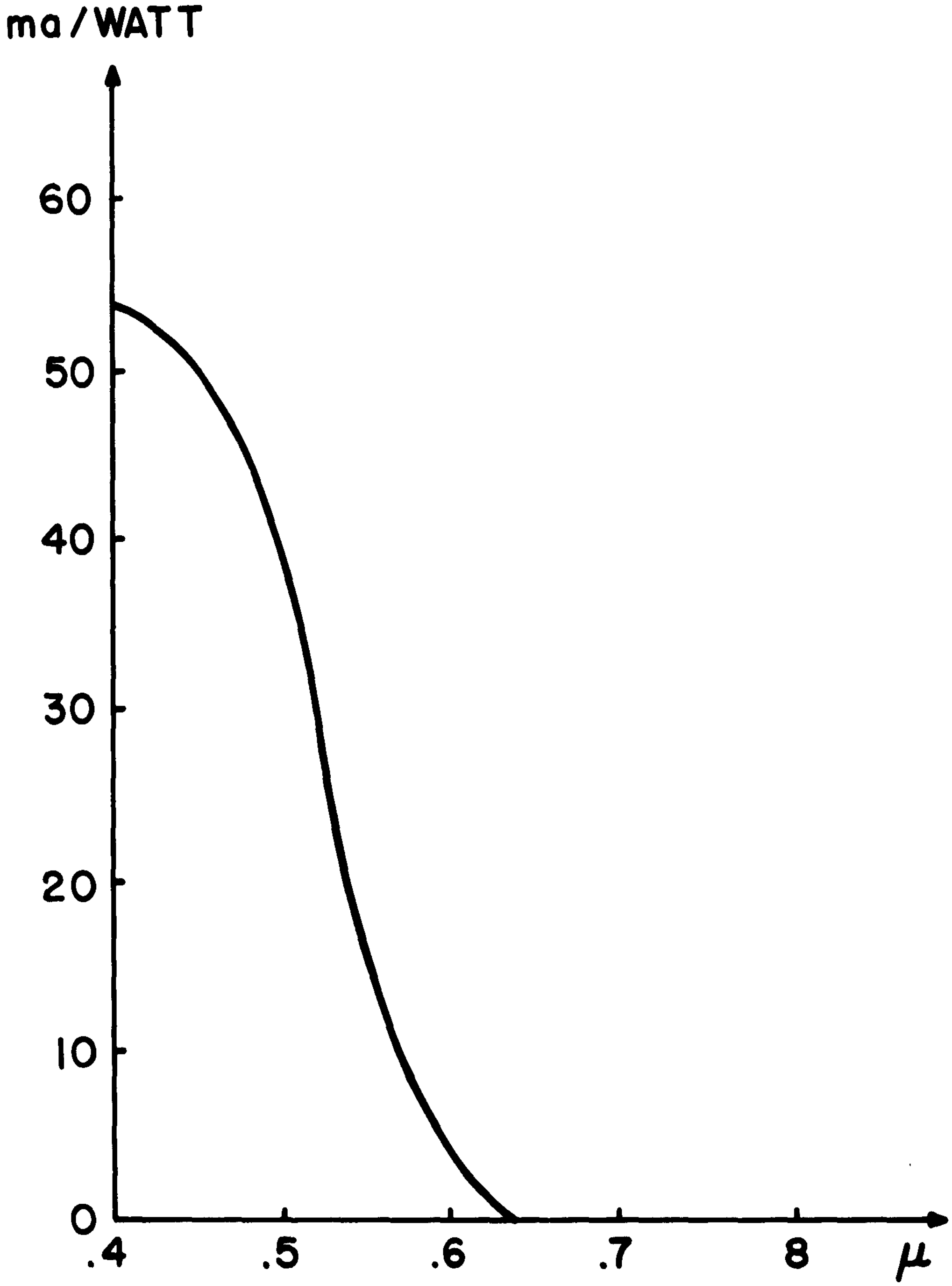

FIG. 1

S-11, K_2CsSb (see above)) the presence of oxygen has proved to be essential or at least beneficial for extended red response. The sole exception to this rule is the S-20 cathode. This unique behavior of the S-20 cathode has always been an incentive to search for a method whereby oxygen can be incorporated with beneficial effect on the long wavelength threshold. Therefore, the following experiments to introduce oxygen were made under this contract.

(a) As was pointed out under (1), the K_2CsSb cathode is improved by superficial oxidation. An attempt was therefore made (VII, p.15) to obtain a better S-20 cathode by processing such an oxidized K_2CsSb cathode with Na. The result of this experiment was disappointing.

(b) The Sb-Cs alternation was replaced in the last stage of the S-20 process by a Cs-oxygen alternation (IX, p.5). This process was partially successful but the final sensitivity was still below that of a conventional S-20 cathode.

(c) Experiments, first proposed by R.G. Stoudenheimer, of the Image Tube Group at RCA-Lancaster, have produced evidence that oxygen improves the sensitivity of S-20 cathodes if it is introduced by exposing the original Sb deposit to a glow discharge in oxygen. A detailed study of this process was undertaken (X, p.11ff, XI, p.10) and led as a by-product to some new and interesting facts about the nature of evaporated Sb films (see Section C) and of the K_3Sb cathode (see Section D) which represents the first stage in the formation of S-20 cathodes.

As far as the effect of the oxidized Sb substrate on the sensitivity of S-20 cathodes is concerned, no final conclusions have been reached at this time. From the results obtained so far it would appear that the maximum sensitivity that can be achieved, both with regard to quantum efficiency and to long wavelength response, is not greater with oxidized Sb substrate but that the average sensitivity is appreciably improved. It will require a larger number of experiments to decide whether this result is statistically significant. Since the oxidation has certainly no detrimental effect it would be well worthwhile to continue with this approach.

3. Miscellaneous New Cathode Compositions

As long as the theoretical understanding of photocathodes is not sufficiently advanced to allow the synthesis of materials with desired characteristics, new cathodes can only be produced on the basis of semi-empirical work of the type that has been successful in the past. The most fruitful approach has been that of replacing chemical elements in a known cathode by other elements of the same column of the Periodic System. This method led to the S-10 cathode (replacement of Sb by Bi) and to the S-20 cathode (addition of alkali metals other than Cs). The only new material of practical importance developed under this contract was the K_2CsSb cathode, described in detail under (1). Many other combinations have been tried; a brief summary of the reasons for each new combination and of the results is given below.

(a) Multi-alkali Cathodes with Rubidium

Including the K_2CsSb cathode, a total of three well defined multi-alkali compounds with high photoemissive sensitivity are known: Na_2KSb, $(Cs)Na_2KSb$ and K_2CsSb. It seems surprising that the alkali metal between K and Cs in the Periodic Table, viz. Rb, is not present in any of these compounds. Therefore, a series of experiments was made in which the K or the Na of the S-20 cathode were replaced by Rb. Using the same nomenclature as in (A), the following sequences were tried (VIII, p.8ff):

(1) Sb-K-Rb at 180°C - Cs

(2) Sb-Rb-Cs-K

(3) Sb-Na-Rb at 220°C - Cs

In all three cases the sensitivity was low and there was no evidence for the formation of a well defined compound. There is no satisfactory explanation for the difficulty of incorporating Rb into a multi-alkali antimonide.

(b) Replacement of Sb by Bi in the K_2CsSb Cathode

Several attempts were made to replace Sb by Bi in the K_2CsSb cathode (IX, p.8ff). A limited success was achieved in that higher sensitivities were obtained than with the mono-alkali compounds Cs_3Bi and K_3Bi. However, the absolute values were so low as to be of no practical interest.

(c) Replacement of Sb by Other Metals During Cs-Activation

During earlier work on the S-20 cathode it had been assumed that the addition of Cs is required to form a superficial Cs film of possibly less than monatomic dimension. However, evidence is increasing that Cs may also be incorporated into the bulk material. In particular, the need for repeated alternations of Sb and Cs in the final stage seems to indicate that an appreciable amount of Cs has to be chemically bound to obtain maximum photosensitivity. It appeared to be at least a possibility that better results might be obtained if elements other than Sb are used to chemically bind the Cs in this alternating process. The following metals were used (VIII, p.10): Bi, Pb, Te, Ag. All except Ag are known to form semiconducting compounds with Cs similar to Sb. Ag was tried because of its beneficial effect on the S-1 and S-10 cathodes. The results of all four experiments were negative.

(d) Incorporation of Silver and Oxygen in Alkali Antimonide Cathodes

Many attempts have been made in the past to combine the high quantum efficiency of alkali antimonides with the long threshold wavelength of the Ag-O-Cs (S-1) cathode. With the development of the process involving an oxidized antimony substrate (2c) a new method of introducing oxygen and silver into antimonide cathodes was provided. Two experiments were made to test this combination (XII, p.26). In the first, the Bi of the Bi-O-Ag-Cs (S-10) cathode was replaced by Sb with completely negative result. In the second, the sequence Sb-O-Sb-Ag-Cs-K-Na was tried and produced cathode sensitivity equivalent to that of a somewhat below average S-20 cathode. The silver seemed to act as a slightly detrimental diluent rather than increasing the long wavelength threshold.

C. Study of Evaporated Antimony Films

During experiments with the oxidation of Sb films by means of exposure to a glow discharge (see B (2)) it was observed that the degree of oxidation, as measured by increase in light transmission and in electrical resistance of the film, depends on the source from which the Sb is evaporated. In some tubes the source consisted of elementary Sb, but in others Sb was evaporated from the intermetallic compound PtSb which releases Sb at a higher temperature and is therefore used in tubes where high degassing bake is essential. To explain the difference between the two Sb sources a systematic study of the resulting Sb films was undertaken. The details are given in X, p.12ff, XI, p.3ff and XII, p.2ff, and the most important results are summarized below.

The Sb deposits evaporated from Sb and PtSb beads, respectively, were compared with regard to the following characteristics.

1. Resistance: Films of the thickness used for cathode formation have infinite resistance at room temperature irrespective of the Sb source. On heating to 160°C, the films produced from an Sb source (type "A") do not change but those from the PtSb source (type "B") decrease to a value in the range of 10^3 ohms.

2. Light Transmission: For equal surface density the light transmission

of "A" is considerably greater than that of "B". In other words, films of equal light transmission contain more Sb per cm^2 if they are deposited from an Sb source rather than from a PtSb source. To give a numerical example, it was found that a film with 75% light transmission contains approximately twice the amount of Sb per cm^2. Further experiments are required to establish the relationship between thickness and light transmission of Sb deposited from a PtSb source over a wider range.

3. Effect of Oxygen: On heating in oxygen to 160°C or on exposure to a glow discharge in oxygen, "B" films show a definite increase in light transmission and resistance, indicating superficial oxidation. By contrast, "A" films do not show any measurable change (the films were made thick enough to produce resistance readings before admission of oxygen).

4. Structure of Sb Films: Samples of "A" and "B" were examined with high energy electron diffraction and with the electron microscope. It was found that the two materials have a similar diffuse diffraction pattern, indicating an amorphous state. The electron micrographs, on the other hand, showed marked differences. Both films consist of individual particles, but the "A" films have relatively wide spaced large particles of about 350 A diameter while the "B" films have close spaced particles of about 30 A diameter. Evidently these differences explain, at least qualitatively, the differences in resistance and light transmission; moreover it is plausible that the smaller particles are more readily oxidized.

5. Molecular Composition of Sb Vapor: To explain the difference in the Sb deposits the hypothesis was put forward that Sb may evaporate as Sb_1 from the PtSb source while it is known to evaporate as Sb_4 from an Sb source. In a preliminary experiment with a mass spectrometer, a spark was produced between Sb-beads and PtSb-beads, respectively. This experiment is only a

substitute for actual evaporation in the mass spectrometer but it showed clearly that Sb_3 and Sb_4 ions are released from Sb and not from PtSb. This result is encouraging confirmation of the suggested hypothesis.

6. Effect of Sb-Substrate on S-20 Cathode: Experiments to correlate the characteristics of S-20 cathodes with the type of Sb source used during the process had only one result of practical importance. Because of the difference in light transmission for equal amounts of Sb per cm^2 the light transmission value to which the original Sb deposit is evaporated has to be lower when a PtSb source is used. Before this difference was known all cathodes made with PtSb source were obviously thinner than intended. Once this difference in optical behavior is taken into account there seems to be no significant effect of the Sb source on the final cathode characteristics.

D. Study of the K_3Sb Photocathode

During experiments on S-20 cathode activation with oxidized Sb-substrate (see B (2)) it was observed that the K_3Sb cathode formed in the first stage of the process differed in visual appearance and in photosensitivity from the K_3Sb cathodes formed from unoxidized Sb. On the assumption that the nature of the K_3Sb cathode may affect the final S-20 cathode a systematic study of the K_3Sb material was initiated. The early results of this work are found in XII, p. 13ff, but additional work done during the last Quarter of the contract has not been reported previously. Therefore, the present status of this project will be discussed in somewhat greater detail.

The K_3Sb cathode was studied with particular emphasis on three properties, viz. light absorption, photoemission and crystal structure. Light absorption and photoemission were measured in an experimental set-up (XII, p.13 and Fig. 8) which allowed comparison of the two types of K_3Sb side by side on the flat window of a single tube.

1. Light Absorption

The light absorption was determined from light transmission measurements disregarding the reflection. In separate experiments it was found that the reflection does not vary appreciably over the wavelength range in which the measurements were made. Therefore, the shape of the absorption curve is adequately represented by (1 - T) where T is the transmission.

The K_3Sb films made from unoxidized Sb look purple in transmitted light while those made from superficially oxidized Sb have a brownish color. Typical absorption curves, made on a tube with quartz windows to extend the curve to greater photon energies, are shown in Fig. 2. The curve for the "purple" material is very reproducible and agrees well with previously published data (see E. A. Taft and H. R. Philipp, Phys. Rev. <u>115</u>, 1583 (1959)). It should be noted that this curve is obtained irrespective of the antimony source, i.e., both from Sb and from PtSb.

An absorption curve for "brown" K_3Sb is also shown in Fig. 2. This curve is not so reproducible in detail but the essential features have been found in all samples. Comparison of the two curves in Fig. 2 shows distinct differences and distinct similarities. The most pronounced difference is the maximum of the purple K_3Sb at 2.47 ev where the other curve has a continuous slope. On the other hand, both curves have a minimum at 2.9 ev, although of differing amplitude. In the U.V. the structure at 3.85, 4.9, 5.2 and 5.8 ev is similar in both curves but the maxima at 3.6 and 4.1 ev of the "purple" material are missing in the other.

The curves in Fig. 2 make the existence of two different modifications of K_3Sb certain. The distinctive structure of the two absorption curves is undoubtedly related to differences in the band structure of the two materials, but it would be a major project to attempt a quantitative interpretation.

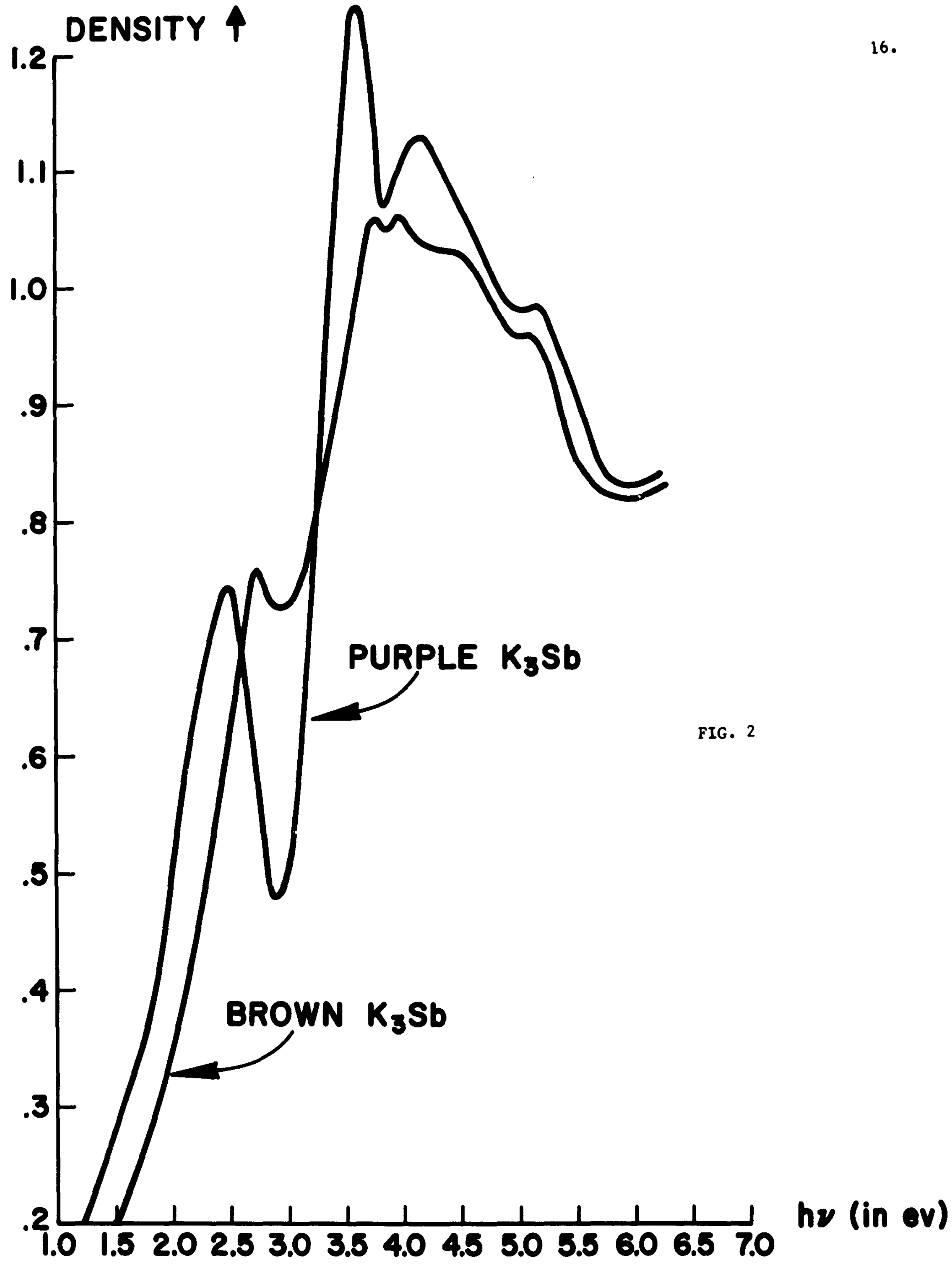
DENSITY
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
PURPLE K_3Sb
BROWN K_3Sb
hν (in ev)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0

FIG. 2

It should be emphasized that so far it has not been possible to produce "brown" K_3Sb without the superficial oxidation of the Sb film, but the amount of oxygen contained in the films must be so minute that the material is still the stoichiometric compound K_3Sb. This has become even more certain from two recent experiments: In the first, brown K_3Sb was obtained with an Sb film evaporated from PtSb which was only exposed to oxygen rather than to a glow discharge in oxygen; in this case no change in light transmission or resistance was measurable (see C) indicating only an extremely small amount of oxygen could have been retained by the film. In the second experiment, brown K_3Sb was obtained from a film evaporated from an Sb source and exposed to glow discharge in oxygen, which -as mentioned before- also produces no measurable change in either resistance or light transmission.

2. Photoemission

On comparing the photoemission of purple and brown K_3Sb three distinct types of photoemissive characteristics were obtained. Standard, i.e., purple, K_3Sb cathodes had the usual sensitivity in the range of 1 μa/l. However, there were two categories of brown K_3Sb. If the Sb film was exposed to K vapor after exposure to oxygen, very low sensitivity was obtained, similar to that of the purple or even lower. On the other hand, if additional Sb was evaporated after exposure to oxygen, the sensitivities were often five to ten times higher. Typical spectral response curves of pairs of purple and brown cathodes in the same tube are shown in Fig. 3. While there is a great spread from sample to sample it can be seen that the unoxidized (purple) portion of the cathode is always inferior to the oxidized portion.

The fact that the brown cathodes with and without additional Sb have identical absorption curves strongly indicates that the two materials are identical in the band structure of the bulk material. The differences in

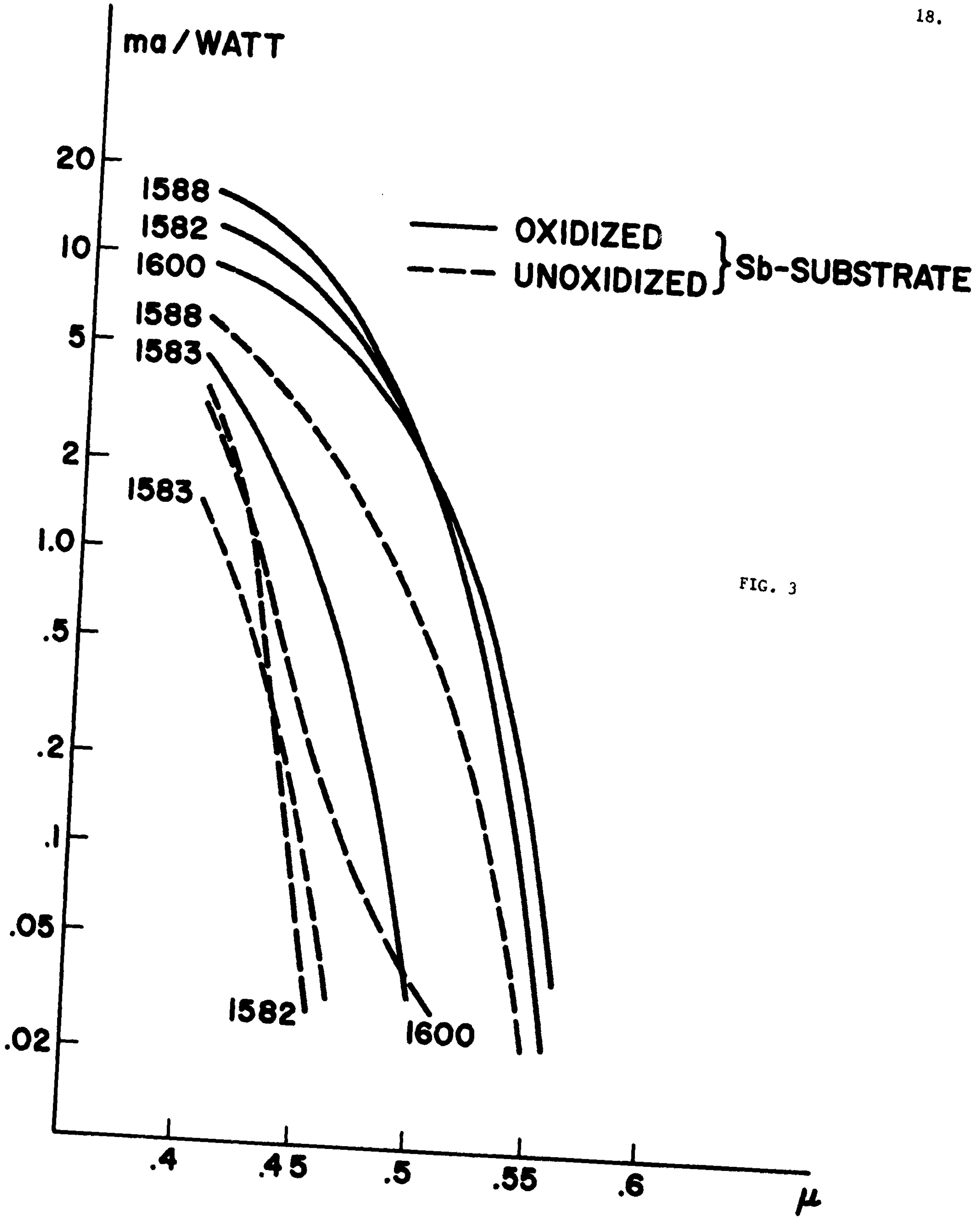
ma/WATT
20
10
5
2
1.0
.5
.2
.1
.05
.02
.4
.45
.5
.55
.6
μ
1588
1582
1600
1588
1583
1583
1582
1600
OXIDIZED
UNOXIDIZED
Sb-SUBSTRATE

FIG. 3

photoemission are likely to be associated with differences in electron affinity and/or band bending.

3. Crystal Structure

As will be reported in more detail under Section IV it has been known for a long time that the purple K_3Sb crystallizes in a hexagonal structure. From the higher sensitivity of the brown K_3Sb made by the sequence Sb-O-Sb-K it was predicted on the basis of earlier experience that this material should have cubic structure. This result was in fact obtained, thus adding another example to the empirical rule that high photoemission is associated with cubic structure. Moreover, it was found that the sensitive K_3Sb is a p-type semiconductor while purple K_3Sb is known to be n-type. This adds to the evidence that p-type conduction is associated with high photoelectric sensitivity.

4. Effect of the Two K_3Sb Modifications on Multi-Alkali Photocathodes

From the previous sections it is apparent that the study of K_3Sb has led to new results of considerable scientific interest. Unfortunately the practical consequences of these results have been disappointing. S-20 cathodes made from either cubic or hexagonal K_3Sb have not shown any statistically significant differences and certainly have not produced any new clues as to the parameter which determines the long wavelength threhsold of the S-20 cathode. The type of K_3Sb base material proved to be equally irrelevant in its effect on the final characteristics of K_2CsSb cathodes.

III. MOLECULAR BEAM FORMATION OF PHOTOCATHODES

A. Introduction

The research program on the formation of photocathodes by deposition of the constituents from molecular beams was directed toward developing a simple, systematic, reproducible method of producing photocathodes. The difficulties associated with the standard processing technique have been described in Part II of this report. The main difficulty with the standard technique is the cumbersome method of obtaining the correct ratio of the constituents. This makes cathode processing relatively non-reproducible and expensive. Furthermore, it is difficult to limit the regions of the phototube which are exposed to alkali metal vapors. The molecular beam method offers the possibility of overcoming these difficulties.

In addition to these practical considerations, the molecular beam method makes possible the quantitative study of the photoemitting system. Because of the small amount of material in a photocathode, it is difficult to vary the cathode constitution in a well defined manner by use of the standard processing technique. By use of molecular beams and the techniques developed for use with them, it should be possible to vary the stoichiometry of a photocathode controllably.

B. Description of the Method

In the molecular beam method, the photocathode constituents are deposited from molecular beams of known flux and cross section. The beams are produced by the effusion method, i.e,, by using molecules from the vapor which exists in equilibrium above the material in condensed form.

According to the kinetic theory of gases, in a closed chamber under equilibrium conditions the number of atoms, N', striking a unit area of the chamber wall is given by the formula:[1]

$$N' = \frac{5.83\text{x}10^{-2}\ L\ P(T)}{(MT)^{1/2}}\ \text{atoms/cm}^2\text{sec} \qquad (1)$$

where

L = Avogadro's number = $6.02\text{x}10^{23}$

$P(T)$ = vapor pressure of the element at temperature T in Torr

M = atomic weight of the element

T = absolute temperature of the chamber

If the chamber has a small aperture of area, a, which is small enough so that the equilibrium condition in the chamber is not appreciably perturbed, those atoms which normally would strike the area, a, are emitted. An atomic beam can be formed by interposing a defining aperture to intercept all atoms except those directed toward the substrate. It has been shown that for molecular beam sources with thin apertures as used in the work reported here, atoms are emitted from the molecular beam source with a cosine distribution. By intercepting all atoms except those in a small solid angle around the normal to the aperture, a molecular beam is formed with a flux of N(atoms/cm^{2}sec) at a distance R(cm) from the aperture where N is given by the following formula:[1]

$$N = \frac{5.83\text{x}10^{-2}\ L\ a\ P(T)}{(MT)^{1/2}\ \pi R^2}\ \text{atoms/cm}^2\text{sec} \qquad (2)$$

It should be noted that the flux is determined only by constants, geometric factors, and the source temperature. Therefore, a constant flux can be achieved simply by keeping the temperature of the molecular beam source constant.

The temperature stability which is required to maintain the beam flux at some predetermined value can be calculated by taking the derivative of N

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[1] I. Estermann, Rev. Mod. Phys. 18, 300(1946).

with temperature, dN/dT:

$$\frac{dN}{dT} = \frac{C}{T^{1/2}}\left(\frac{dP}{dT} - \frac{P}{2T}\right) \tag{3}$$

where C includes all terms in (2) other than temperature or pressure. The vapor pressure of an element can be described by the following equation:[2]

$$\log P = A - \frac{B}{T} \tag{4}$$

Putting (4) into (3), the following expression results:

$$\frac{dN}{N} = \left(\frac{B}{T^2} - \frac{1}{2T}\right) dT \tag{5}$$

For the case of Cs,[2] B = 9198. Therefore, at T = 450°K, in order for the flux to be kept constant to within 1%, the temperature must be kept constant to within 0.2°K.

While the molecular beam source can control the rate at which atoms are incident at the substrate, the stoichiometry of a cathode can be controlled only if all (or a known fraction) of the incident atoms are incorporated into the cathode. Incident atoms will not be included in the cathode if either they are reflected at the surface or they are desorbed from the cathode. Experiments indicate that metal atoms are generally not reflected when incident on a metal layer, although a metal atom incident on a glass substrate may be reflected.

In experiments conducted under this contract, it was shown that good agreement could be obtained between the rate of deposition of Sb calculated from equation (2) and the rate calculated from the measured weight of the material deposited on glass substrates at room temperature assuming that all incident atoms stick. (II-10, V-9) Furthermore, it has been shown that satisfactory agreement could be obtained between calculated deposition rates

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[2] S. Dushman, Vacuum Technique, J. Wiley & Sons, Inc., New York, 1949, Chapter 4.

and those derived from mearsurements of optical transmission (VII-2).

In the experiments on molecular beam formation of cathodes, either Sb was evaporated first on glass or Sb was deposited simultaneously with alkali metal atoms. In the first case, as indicated above, reflection of atoms does not seem to be a problem. In the latter case, it is expected, because of the reaction between the alkali and antimony, that a non-volatile compound is formed. Therefore, reflection of the deposited material should not be a problem.

The desorption of the cathode constituents may be a problem, in particular, the alkali metals which may build up on the surface of the cathode, if compound formation between the alkali atoms and antimony are diffusion limited. This may be the case when the cathode constituents are deposited sequentially. Although the importance of this effect will depend upon the extent of the reaction between the alkali and antimony, a lower limit to the mean time which an alkali atom will remain on a surface will be given by τ, the mean time that an alkali atom will remain on the surface of bulk alkali metal. This time can be calculated from the following equation:[3]

$$\tau = (2\pi kTm)^{1/2} \frac{\sigma_1}{P_{Torr}} \quad \text{(sec)} \qquad (6)$$

where σ_1 is the density of sites on the metal surface. Similarly, the rate of desorption can be calculated from the following:[4]

$$G = 5.833\text{x}10^{-2} \, P_{Torr} \sqrt{\frac{M}{T}} \quad (\text{grams/cm}^2\text{sec}) \qquad (7)$$

These quantities are evaluated for Cs, Na, and K for $T = 300^{\circ}K$ and $\sigma_1 = 10^{15}$ atoms/cm^2 in the following table.

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[3] I. Langmuir, J. Am. Chem. Soc. 54, 2798(1932).

[4] S. Dushman, Ibid, pg. 17.

Atom	τ (sec)	G (grams/cm^{2}sec)
Na	2.36×10^4	4.46×10^{-13}
K	1.57×10^2	4.71×10^{-10}
Cs	6.16	1.58×10^{-6}

For the case of sodium and potassium, the evaporation rates are small and can probably be neglected if deposition rates such that a cathode is formed in 10 minutes or less are used. As will be discussed below, the work performed under this contract has been primarily concerned with the formation of Na_2KSb. In the case of Cs_3Sb, direct measurements show that all incident atoms are absorbed as long as the ratio of atoms of Cs to Sb is less than three to one (III-4, IX-29).

C. Mono-alkali Antimonides by Sequential Deposition

The study of mono-alkali antimonides is a natural starting point for the development of techniques for molecular beam formation of photocathodes. Because of the relative simplicity of these materials especially compared to the multi-alkali phases, it is possible to investigate some of the finer points of cathode formation. Emphasis in this phase of the work was placed on Cs_3Sb; however, experiments with Na_3Sb and K_3Sb have also been performed.

Mono-alkali antimonide cathodes have been produced by depositing antimony by evaporation from an Sb bead and then using a molecular beam gun to deposit the alkali metal until peak photoemission was achieved. The Sb thickness, as has usually been estimated from transmission measurements, has been of the order of 4 μgrams/cm^2. On several occasions, the substrate has been heated during alkali metal deposition.

In general, cathodes have been deposited which have sensitivities comparable to those produced by conventional processing. Cs_3Sb cathodes with sensitivities of 15 μa/lumen (IV-8), K_3Sb cathodes with 3 μa/lumen (III-9), and Na_3Sb cathodes with $4x10^{-2}$ μa/lumen (III-11) have been produced.

Measurements made during the processing of Cs_3Sb indicate that diffusion plays an important part in the cathode formation. For example, usually peak photoemission is obtained by depositing more cesium than is required for immediate maximum response and then allowing the substrate to stand with no further addition of cesium. The sensitivity obtained in this way is higher than that which occurs while cesium is being deposited. The need for cesium beyond the peak during deposition is interpreted to be the result of non-uniformity in the cathode composition. The peak in emission which occurs upon standing is the result of diffusion which causes the cathode to become uniform. Desorption may also play a role in this process.

The peak in photoemission can also be achieved by heating the substrate (V-6 to 8). However, heating does not result in higher sensitivity cathodes. At the higher temperatures used (up to $100^{\circ}C$), the non-uniformity in composition still exists. At higher temperatures, desorption of alkali metal may be important.

An estimate of the ratio of Cs to Sb required to obtain peak photoemission was made when a Cs-Sb cathode was produced on a quartz crystal (IX-27) at room temperature. These results indicate that the ratio for peak sensitivity is 2.79 to 1. In this experiment, the Cs was deposited from the vapor at room temperature rather than by means of a molecular beam, but the effects should be the same. This experiment also indicated that Cs incident on the quartz crystal was entirely adsorbed until the ratio of Cs to Sb exceeded 3 to 1.

An estimate has been made of the accuracy with which the ratio of alkali to antimony must be controlled in order to obtain high sensitivity. In one experiment, Cs from a molecular beam was deposited on a cathode which had reached equilibrium (V-8). Adding 1.4×10^{14} Cs atoms/cm^2 reduced the sensitivity by a factor of 2. In the experiment described above, in which the cathode was produced on a quartz crystal (IX-27), it was observed that the photoemissive sensitivity decreased by a factor of 2 when the cesium content was increased by 5% beyond the amount of cesium which gave peak sensitivity. The interpretation of these results is confused by the effects of diffusion; however, they indicate that the cathode constituents must be very accurately controlled.

Measurements of photoemission as a function of time as alkali metal was deposited on antimony, show that the rate of increase is a function of composition and does not go up at a uniform rate (III-9 to 11). This effect may, in part, be the result of variations in the resistance of the cathode which prevents saturation of the photoemitted electrons (IV-5). In any case, it appears that measurements of photoemission and resistance during alkali deposition would be useful in evaluating the formation of cathodes.

Electron diffraction studies of the mono-alkali antimonides produced by sequential deposition with molecular beams showed that they are single phase systems having the same structure as cathodes produced by conventional processing (VIII-20, IX-16).

D. Multi-Alkali Antimonide Cathode Formation by Sequential Deposition

Attempts have been made to produce multi-alkali antimonide photocathodes of high sensitivity by depositing the constituents sequentially. These experiments were conducted in tubes in which a moveable substrate could be placed before molecular beam sources of Na, K, or Cs, or an evaporation bead of Sb. The results of these experiments indicate that sequential deposition on room temperature substrates does not result in a high sensitivity cathode.

In the first experiments, light transmission was used to measure the antimony deposits. The molecular beam temperatures were adjusted in an attempt to obtain the correct ratio of Na and K, the total alkali metal being controlled so that its ratio to Sb was 3 to 1. In each case, low sensitivity resulted (IV-2).

Subsequently, attempts were made to produce first a mono-alkali antimonide cathode and then add the second alkali and antimony alternately in small steps so that a composition Na_2KSb would result. The results are summarized below:

Report No.	pg.	Tube No.	Deposition Description	Sensitivity
IV	4	S-1281-4	Sb-Na to Na_3Sb, alternated K and Sb	low
IV	6	S-1285-1	Sb-K to K_3Sb, alternated Na and Sb	5 μa/1
IV	6	S-1285-2	Same as S-1285-1, thinner Sb	3.5 μa/1
IV	6	S-1285-3	Sb-Na to Na_3Sb, alternated K and Sb Added Cs to S-1285-3	16 μa/1 90 μa/1
IV	7	S-1289-1	Sb-K to K_3Sb, alternated Na and Sb	low
IV	8	S-1289-2	Sb-Na to Na_3Sb, alternated K and Sb	5 μa/1
IV	8	S-1289-3	Sb-Na to Na_3Sb, Cs, K, Sb	low
IV	8	S-1289-5	Na-Sb to Na_3Sb, K, Sb, Na	4.5 μa/1

These experiments indicate that a multi-alkali effect can be achieved occasionally in a small area, but usually cathodes with sensitivities much below those produced by standard processing were obtained. This occurred despite the fact that, by the technique of adding the second alkali and alternating it with Sb, the correct ratio of the constituents must have been achieved, at least in some cases.

Experiments were performed to evaluate the effect of a moderate increase in the substrate temperature on the cathode formation. The cathode temperature was estimated to be 130°C. The results of these depositions are summarized below:

Report No.	pg.	Tube No.	Deposition Description	Sensitivity
IV	9	S-1292-1	Sb-Na to Na_3Sb, alternated K, Sb	13 μa/l
IV	10	S-1292-2	Sb-K to K_3Sb, alternated Na, Sb	15 μa/l
IV	10	S-1292-3	Sb-Na to Na_3Sb, K, Sb, Cs	40 μa/l

Although higher average sensitivity resulted when the substrate was heated, the sensitivities are considerably lower than can be produced by standard processing.

The probable reason for this low sensitivity has been revealed by observations of the crystal structure of the molecular beam depositions. The crystal structure has been studied by use of high energy electron diffraction.

It is well known from x-ray studies of the multi-alkali antimonide as well as the mono-alkali antimonide crystal structures that the efficient emitters (S-11, S-20) have cubic crystal structure while the lower sensitivity material such as Na_3Sb, K_3Sb and K_2NaSb have hexagonal structures. In the formation of S-20 photocathodes by sequential deposition by use of the molecular beam method, a low sensitivity hexagonal phase must necessarily be produced initially. A high sensitivity photocathode cannot be produced if the transformation from a hexagonal to cubic phase does not take place.

Photocathodes were deposited by means of molecular beam sources on thin amorphous carbon substrates which could be moved into the path of an energetic electron beam. The cathodes were produced following the general procedures described above but with their electron diffraction patterns being investigated at various times during the processing (VIII-16, IX-15).

The results of the electron diffraction examination of cathodes made by sequential deposition from molecular beams showed, in general, that the

the final cathode consisted of two or more phases and that as the cathodes became thicker, it became more difficult and usually impossible to convert them to one phase. Typical observations are summarized below:

(1) Failure to convert Na_3Sb to Na_2KSb upon addition of K and Sb resulting in a mixture of K_3Sb and Na_3Sb.

(2) Formation of cubic multi-alkali Na_2KSb containing lesser amounts of either Na_3Sb or NaK_2Sb.

(3) Conversion of K_3Sb to hexagonal NaK_2Sb upon addition of Na and Sb followed by failure to convert this phase totally to cubic Na_2KSb upon addition of Na and Sb.

(4) Observation of only cubic Na_2KSb.

(5) Formation of Na_2KSb or NaK_2Sb containing unidentified phases.

(6) Changes in the diffraction pattern with time, some which could be identified while others could not.

These results indicate that the reaction kinetics including diffusion and phase change are too slow at room temperature for a homogeneous compound to form. It is concluded that this is the reason for the failure to produce high sensitivity multi-alkali photocathodes by sequential deposition on room temperature substrates. The conversion to a single phase apparently takes place more readily in a mono-alkali antimonide system.

E. Multi-alkali Antimonide Cathode Formation by Simultaneous Deposition

It should be possible to overcome the difficulties described above by depositing the cathode constituents simultaneously. By this means, the cathode material would be uniformly dispersed from the beginning of the deposition so that little or no diffusion would be necessary. In addition, the composition required to produce the cubic Na_2KSb phase which is associated with high photosensitivity would be available from the start so that no stable hexagonal form should develop which must then be converted into the cubic form.

It became apparent almost immediately after simultaneous deposition experiments were started that much better control of the deposition rates would be necessary for simultaneous depositions than for sequential deposition. Most of the recent effort on formation of cathodes by simultaneous deposition from molecular beams has been directed toward obtaining stable, well-controlled beams of Na, K, and Sb atoms.

The first experiments were attempts to make photocathodes by a quasi-simultaneous deposition method (VI-6). In these experiments, a cylindrical substrate was rotated before molecular beam sources of Na, K, and Sb. Since less than one monolayer of each constituent was deposited in each cycle, intimate mixing comparable to that obtained by simultaneous deposition should result. Difficulties with maintaining stable rates as well as with adjusting the rates to the correct values were evident (VII-4, VIII-15). As a result of these experiments, it was decided that an independent means of measuring deposition rate was required if control adequate for simultaneous deposition was to be achieved.

Considerable effort has been expended to develop a quartz crystal oscillator mass detector for use in the formation of photocathodes. This development included a mount which can be baked in vacuum and a stable circuit for use with the crystal oscillator. The sensitivity of the quartz crystals and mount used is approximately 25 cps/μgram/cm^2. The frequency stability is ±1 cps over a three hour period (X-20). Mass changes as small as .05 μgrams/cm^2 or of the order of 0.1 atom layer can be detected.

The quartz crystal was incorporated into a tube such that molecular beam sources of Na, K, Sb, and Cs could be directed at it sequentially or simultaneously. Photocathode constituents could be deposited simultaneously on a series of substrates which could be moved in front of the quartz crystal. This tube was used by first adjusting the molecular beam deposition. rates sequentially and then depositing the constituents on the substrate simultaneously (IX-21). Experiments with this type of tube indicate that sensitive cathodes may result if at least partial simultaneous deposition is used (IX-25 to 27), although this does not appear to be a sufficient condition (XI-19).

Experiments with this tube have shown that the rate of effusion from the glass molecular beam sources used for the previous experiments were not in agreement with the rates calculated from equation (2) for sodium and potassium. This difficulty has tentatively been attributed to the reaction of the alkali metals with the glass which limits the vapor pressure above the bulk alkali metals (XII-27).

Because of this difficulty and, in addition, because it has been extremely difficult to adjust the deposition rates because of thermal lag in the glass, new all-metal molecular beam sources have been developed (XII-28) as well as a circuit which has been used along with a quartz crystal (XII-29). to obtain stable deposition rates.

During the last quarter of this contract, a new experimental tube has been tested. This tube is shown in Fig. 4. It consisted of three all-metal molecular beam sources, Sb, Na, and K, made from .002"-wall stainless steel tube, 1/8" in diameter. Alkali metal was distilled into the guns through a copper tube which was then pinched off. The tops of the guns were covered by a .001"-thick stainless steel sheet. The guns were opened by puncturing the cover sheet by means of a needle on a rod which could be moved by means of a bellows. Directly above each gun was located a quartz crystal oscillator. The aperture plate limited the region on which the

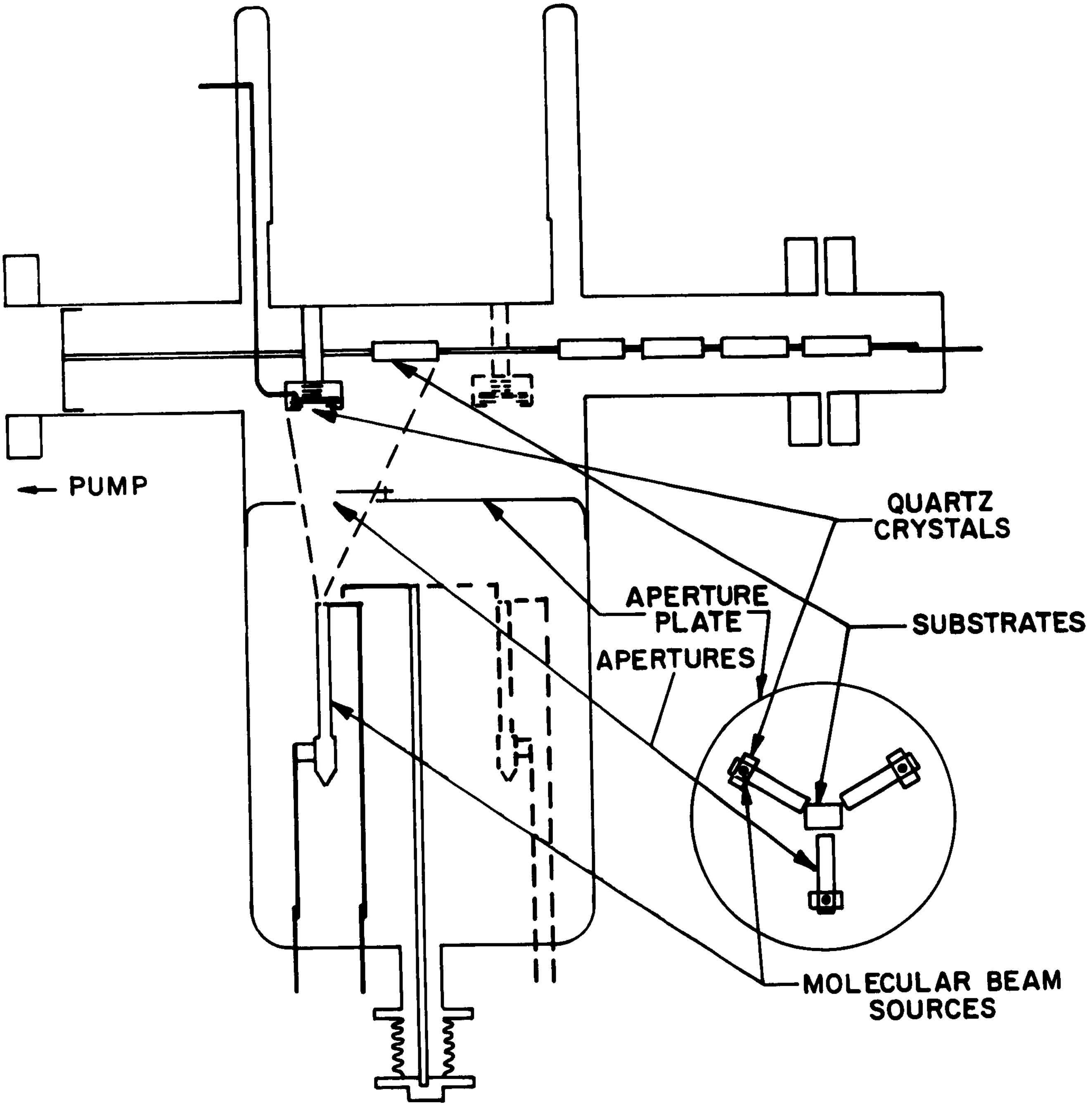
PUMP
QUARTZ CRYSTALS
APERTURE PLATE
SUBSTRATES
APERTURES
MOLECULAR BEAM SOURCES

FIG. 4

elements could be deposited to the axis of the tube where a substrate could be placed or to the crystal directly above the source. The substrate thus received the cathode constituents from the three sources while each crystal received only the element from the source directly below. Aperture shutters could cut off that part of each beam directed toward the substrate.

The deposition rates were controlled by the feedback system shown schematically in Fig. 5. This circuit measures the frequency of each quartz crystal oscillator and controls the power to the associated beam source so that the frequency changes linearly at a predetermined rate. The ratio of the deposition rates can be controlled by means of ratio control potentiometers to a high degree of accuracy. The low thermal mass of the molecular beam sources makes possible rapid response and therefore accurate control.

In the initial experiments, the rates were adjusted to values such that 5 μgrams/cm^2 of Sb would be deposited in 7.5 minutes and such that the Na and K deposition rates would be .377 and .319, respectively, that of Sb. The assumption was made that the sensitivity of all quartz crystal oscillators was the same.

The control circuit worked exceedingly well, maintaining the desired values for the frequency change within measuring accuracy.

Two cathodes (Na-K-Sb) were produced which had low sensitivity after simultaneous deposition but which could be brought up to a sensitivity of 10 μa/lumen after sequential deposition steps. Formation of a K_3Sb cathode by sequential deposition indicates that the K to Sb deposition rates are almost exactly those required. However, there is evidence to indicate that the Na deposition rate was too high, indicating that the Na crystal sensitivity was too low.

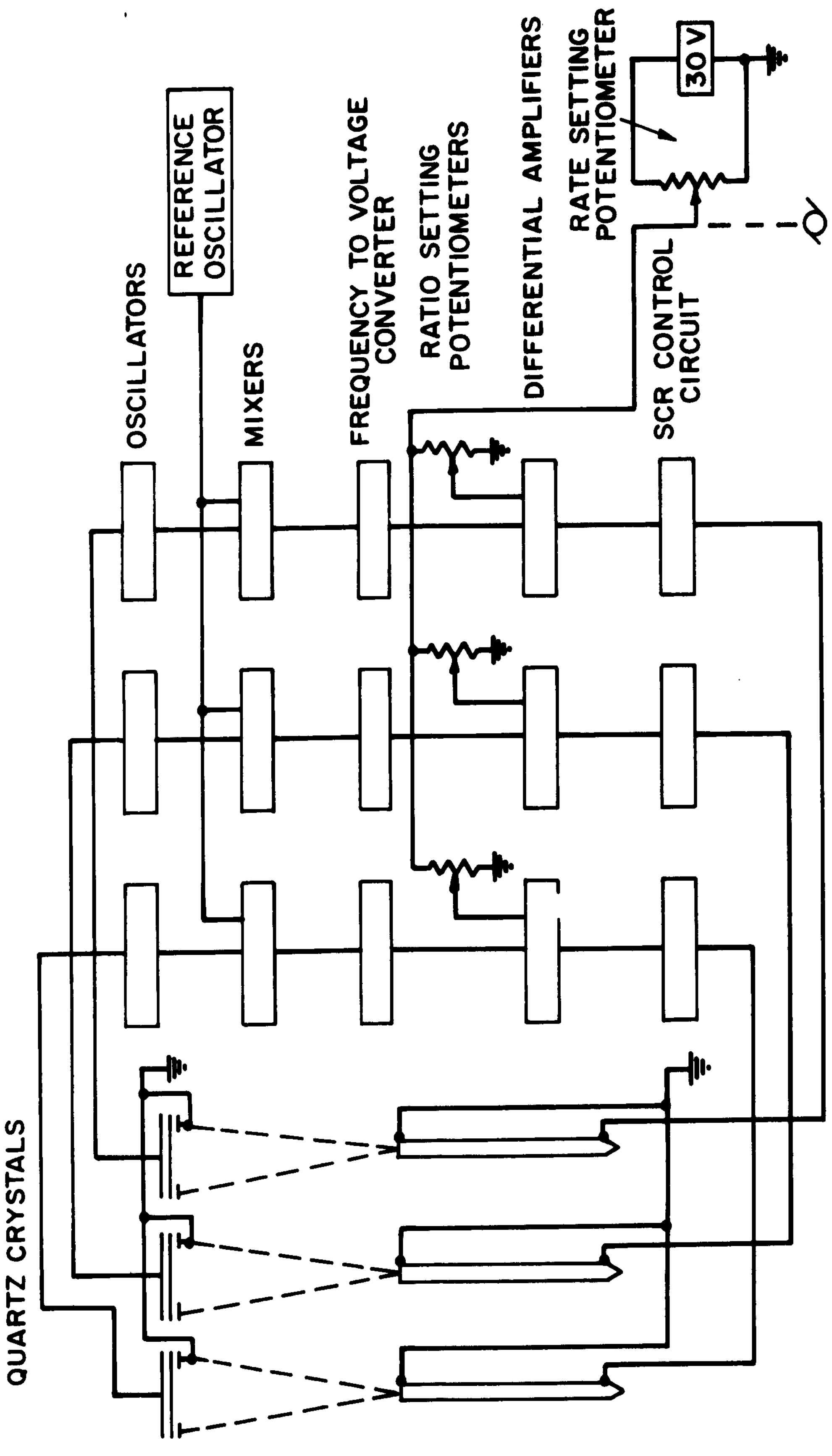
QUARTZ CRYSTALS
MOLECULAR BEAM SOURCES
OSCILLATORS
REFERENCE OSCILLATOR
MIXERS
FREQUENCY TO VOLTAGE CONVERTER
RATIO SETTING POTENTIOMETERS
DIFFERENTIAL AMPLIFIERS
SCR CONTROL CIRCUIT
RATE SETTING POTENTIOMETER
30 V

FIG. 5

The lack of uniformity in sensitivity of the quartz crystals appears to have limited the results of this experiment on simultaneous deposition. In future experiments, this difficulty can be eliminated by use of a second Sb molecular beam source which can deposit equal amounts of material on all crystals simultaneously and can thereby be used to measure their relative sensitivities. Any differences can be taken into account when the deposition ratios are selected.

The results with this tube are highly encouraging. In the future, it should be possible, by simply adjusting a series of potentiometers, to adjust the deposition rates with a high degree of precision to any value desired. It should, therefore, make it possible to exploit fully the potential of the simultaneous deposition method without further development of new techniques.

F. Preparation of Cathodes Using Ion Sources

Initial experiments using synthetic zeolites as ion sources for the preparation of photocathodes were described in the previous report of this project (XII, p.49). The use of a controlled ion source offers the possible advantages of electronic control of the rate and direction of the deposition as with molecular beams produced by the effusion method described above and eliminates the problems of generation and control of the corrosive metals themselves.

In the initial experiments a platinum clad molybdenum filament was coated with the desired zeolite by fusing it to wire. This type of source was used to produce a cathode, supposedly K_3Sb, of 12 μamps/lumen. However, the relatively high red response of the cathode indicates that some portion of the cathode may actually be Na_2KSb. Spectrographic analysis did indeed show that up to 20% of the alkali atoms present were sodium ions. By increasing the number of exchange cycles, described in (XII, p.50) it was possible to produce a source containing approximately 90-95% potassium ions from Linde Type 4A pelletized and powdered molecular sieves.

The pellets were chosen in preference to the powders because of their obvious advantages in handling. They were heated conveniently by wrapping a spiral of 0.015" platinum clad molybdenum wire around them. However, no ion emission was observed from any of the pellets tried (Na Linde 4A, K exchanged 4A and Cs exchanged 13X). It was concluded that the silicate binder later found to be present in these pellets effectively kills the ion emission without materially impairing the more conventional functions of these materials.

On the basis of that experience it was decided to use powder sources to coat or fill wire spirals which could be resistively heated. To facilitate handling and to lessen scaling and sintering problems an organic binder formula similar to that used for coating wires with oxide cathode materials was employed. The use of these binders gave a coating which adhered moderately well to the filament after an initial bakeout in air and a final bakeout in vacuum at red heat. However, several attempts to prepare cathodes using these sources have resulted in cathodes of sensitivies considerably less than normal. In addition, the cathodes appear to be more opaque than should be the case for the initial thickness of Sb and their color is not characteristic of the cathodes in question. It is believed that an undetermined portion of the binder or its decomposition product remains behind after the vacuum degassing of the zeolite. It is believed that this residue is then deposited on the cathode substrate when the cathode is heated to the higher temperatures necessary to attain ion emission, thus effectively lowering the photoresponse of the cathode. An alternative possibility is that the presence of the residual binder hastens the decomposition of the zeolite itself and that its deposition on the cathode substrate is responsible for the increased opaqueness and loss of sensitivity of the cathode.

The results of these preliminary experiments are considered sufficiently encouraging to warrant further development of ion sources for the production of sensitive photoemitting surfaces.

IV. STRUCTURE STUDIES

A. Structure of Photocathodes

1. Introduction

A study of the crystal structure of photocathodes has been carried out under the contract as part of the effort to obtain data concerning the nature of efficient photoelectron emitting materials. The basic cathodes studied include the S-20 cathode, $Cs:Na_2KSb$; the bialkali cathodes, Na_2KSb and K_2CsSb; the binary alkali antimonides of potassium, rubidium, and cesium; and the composite cathodes Ag-Cs-O and Ag-Bi-Cs-O. During the course of this investigation, the existing techniques for x-ray analysis of photocathodes were improved upon and an electron diffraction apparatus was constructed so that the photocathodes could be examined without having to be destroyed. A brief description of the apparatus is given as well as a summary of results for the various photocathodes. References are given to the more detailed descriptions given in the quarterly reports of this project.

The x-ray diffraction method was the first to be developed and is of particular advantage where one wishes to obtain accurate diffraction data (e.g., lattice constants, intensity data, shape of the diffraction line, etc.). However, the most commonly used technique is a one-shot process in which the photocathode is destroyed as such in obtaining a sample for diffraction analysis. In addition, it is usually necessary to make the cathodes several times thicker than the normal semitransparent variety in order to obtain a sufficient sample. This presents no problems for the binary and bialkali cathodes which are apparently homogeneous but, in the case of the composite cathodes and perhaps the S-20 cathode where the properties of the cathode are markedly affected by the thickness (by factors other than simple absorption), the technique is of questionable value.

On the other hand, the use of electron diffraction permits the photocathodes to be examined non-destructively as thin films of normal thickness. In addition, the cathode processing may be stopped at any point and the diffraction pattern examined. This was used to particular advantage to elucidate the nature of the phases formed during the processing of cathodes using the molecular beam technique. Because the angular dispersion of the diffraction limes is considerably smaller for electrons than for x-rays, the resolution of the electron diffraction pattern is inferior to that of the x-ray pattern (unless an extremely long tube is used). In addition, it is necessary to use a special substrate for transmission electron diffraction (usually amorphous carbon). This substrate may, in special instances, affect the response of the cathode but, in general, this was found not to be the case. However, a more serious problem seemed to be in preparing photocathodes of normal response. This is not surprising in light of the fact that the optimization of photocathode response is largely an empirical process and differs for different tube geometries. This was a less serious problem in the x-ray diffraction tubes where the processing conditions and geometry more closely approached those existing in the experimental spherical cathode bulbs.

In summary then, the x-ray technique is preferable where accuracy of the data obtained is of prime importance or in cases where a cathode of optimum response is required. Electron diffraction must be used in cases where a thickness limitation is imposed or for the monitoring of cathode processing. A brief description of the various apparatus is given below.

2. Apparatus

A so-called scraper tube was used for most of the x-ray diffraction work. The tube is designed so that a portion of the photocathode, prepared on a glass, can be removed from the substrate by scraping with a razor blade whose motion is controlled externally by means of a bellows. The material removed from the substrate is allowed to fall into a capillary tube sealed onto the main tube directly below the substrate. When a sufficient quantity of sample is obtained, the capillary is sealed off from the tube and reserved for x-ray analysis. The initial tube employed a substrate situated in the interior of the tube (I-9). The tube was later modified so that the cathode substrate was a part of the exterior wall in order to more closely duplicate the conditions existing in the standard spherical bulbs. In addition, Varian flanges were used to connect the bellows and press assemblies to the tube to facilitate rebuilding of the tubes after each experiment. A photograph of this tube is shown in Fig. 6.

A second type of tube for x-ray diffraction studies was built in order to overcome the thickness limitation discussed above. The tube had two coaxial thin mica or FN glass windows. One window served as part of the cathode substrate and the other served as an x-ray entrance port. The tube was properly alligned on an x-ray unit and the diffraction data collected on a flat film placed in front of the exit window. This tube was used primarily to examine Ag-Bi-Cs-O cathodes (II-14; III-18). The long exposure times necessary, the high background on the films due to the windows, and the limited amount of data that could be obtained were serious drawbacks to this technique which eventually led to its replacement by the more versatile electron diffraction method.

FIG. 6

A description of the original transmission electron diffraction tube is given in the Fifth Quarterly report of this project and subsequent modifications are given in later Quarterly Reports. A detailed summary and description of the tube with these modifications are given elsewhere.[5] The only significant change made since is to modify the power supply so that the electron gun is operated at the high voltage while the target and phosphor screen are at ground. Satisfactory operation up to 55 KV has been achieved when the gun end of the tube is immersed in an oil bath. Satisfactory operation up to 37 KV has been achieved in air. Accelerating potentials of 30 to 35 KV have been satisfactory for most purposes.

A reflection electron diffraction appartus was also built and tested (X-25). The original purpose of this tube was to allow direct examination of the photocathode made on a normal substrate. Although diffraction patterns were obtained using this apparatus (XI-27; XII-48), an extremely high background was observed and the quality of the lines was coarse and diffuse. It was obvious that unless sharper patterns could be obtained, this technique would be of little value except under the most ideal conditions. A possible use of this tube would be in conjunction with a vertical molecular beam deposition apparatus.

3. Structural Data for Alkali Antimonides

The normal valent alkali antimonides and bismuthides are characterized by either a hexagonal or cubic crystal structure. Various degress of order have been observed for the cubic form which include the completely ordered DO_3 type, the partially ordered B32 type and perhaps a completely disordered A2 type.

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[5] W. H. McCarroll and R. E. Simon, Rev. Sci. Instr. <u>35</u>, 508-11(1964).

The hexagonal polymorphs are described completely by the Na_3As structure type, see Fig. 7, found by Brauer and Zintl.[6] For Cs_3Sb, only cubic modifications have been observed while for Na_3As only the hexagonal form has been found. The remaining Li, K, and Rb compounds are polymorphic displaying either the hexagonal or cubic structures depending upon the method and temperature of formation. A thermal analysis[6] has been carried out only for Li_3Sb and has shown that the cubic form is the high temperature form. In the case of the bismuthides only K_3Bi is known to undergo a polymorphic transition and again the high temperature form is the cubic form. Thus, although the cubic form appears to be the high temperature form, it is possible to stablize it below its transition temperature if it is prepared as a thin film.

The cubic crystal forms are all derived from the following set of free centered cubic positions:

(a) $0,0,0$
(b) $\frac{1}{4},\frac{1}{4},\frac{1}{4}$
(c) $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
(d) $\frac{3}{4},\frac{3}{4},\frac{3}{4}$

all + $(0,0,0;\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2};\ \frac{1}{2},\frac{1}{2},0)$

In the DO_3 structure, the antimony atoms are in (a) and the remaining positions are occupied by the alkali metal. The B32 type structure is characterized by partial order in which the (a) and (b) positions are occupied by alkali metal and the (c) and (d) positions are populated by equal amounts of alkali metal and antimony.(see Fig. 8). In the disordered structure (which may exist for Cs_3Sb), all positions are occupied randomly by alkali metal and antimony. (The true unit cell is then body-centered with repeat distance one-half that of the original face-centered cell.)

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6. G. Brauer and E. Zintl, Z. Phys. Chem. 37B, 323(1937).

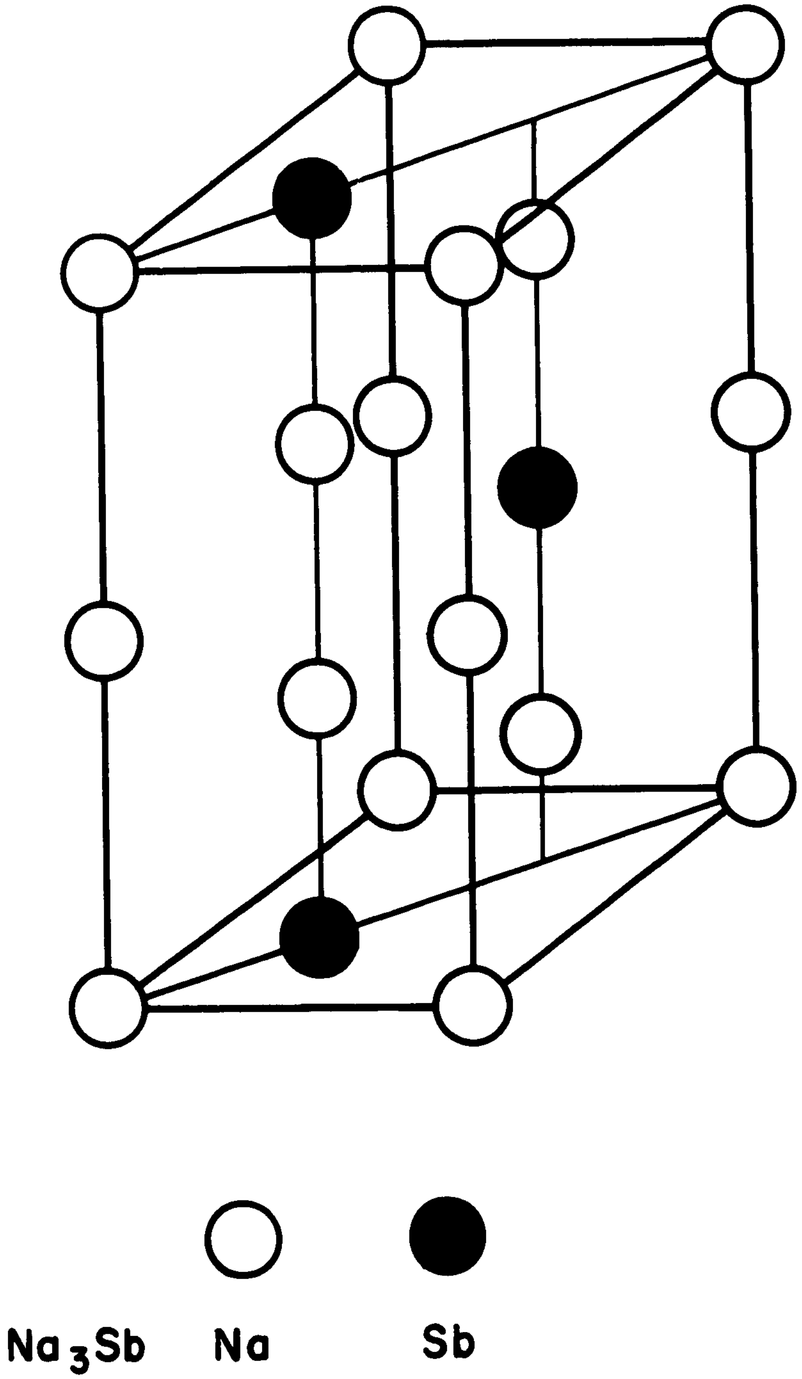

FIG. 7

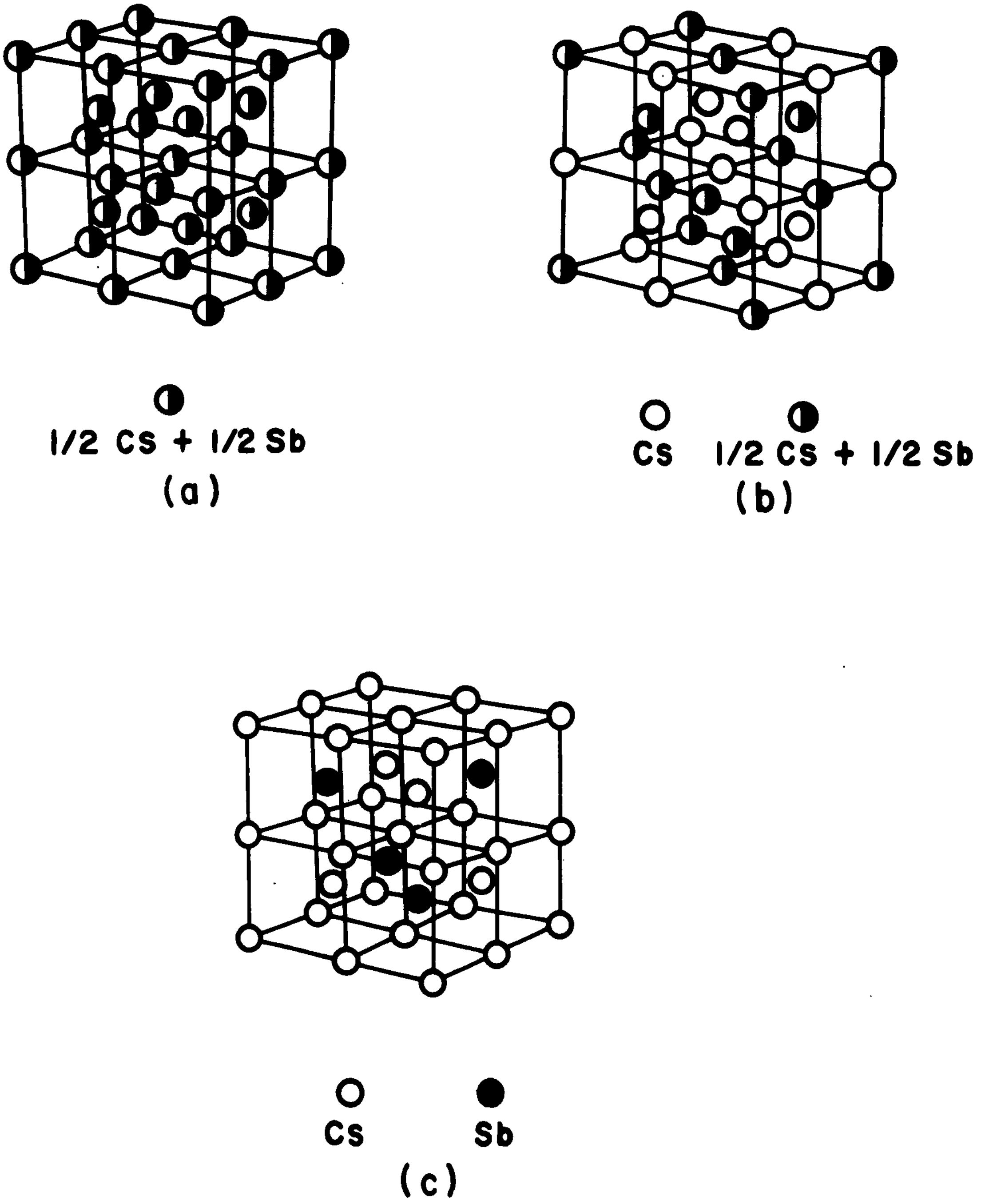

FIG. 8

The bialkali antimonides, Na_2KSb and K_2CsSb, have the ordered $L2_1$ structure which is derived from the above positions by placing the antimony at (a), the numerically dominant alkali metal in (b) and (d), and the remaining alkali metal in (c).

A summary of crystallographic data from both these and other laboratories is given in Table I. A more detailed description of the work on cubic K_3Sb is given below since this work has only recently been completed.

Structural data for the alkali antimonides studied in this Laboratory have been obtained from both powders and from actual photocathodes. In the past, the necessary intensity data for the structure determination were obtained either from the powders prepared above 200°C or from photocathode samples which had been sealed in capillaries and annealed several days at temperatures ranging from 200-250°C. This was done to sharpen the diffraction lines in order to obtain an accurate measure of their intensity. It is, of course, recognized that the annealing process could influence the ordering. However, an argument has been given in previous reports which shows that this is not likely to have been the case where annealing to K_2CsSb has been applied. For cubic K_3Sb, it was not possible to anneal the sample without inducing the transformation to the hexagonal modification. In this case, analysis of the intensity data from the unannealed samples shows that it has an essentially ordered DO_3 structure although there is good reason to believe that there may be some departure from complete order. A more complete investigation of this as well as an analysis of intensity data from other alkali antimonide photocathodes would constitute a logical extension of this work.

The following significant points emerge from an examination of the results in Table I. (1) All of the materials investigated except Na_3Sb can be prepared as photocathodes with cubic crystal structures whose photoemission

TABLE I - SUMMARY OF STRUCTURAL DATA FOR NORMAL VALENT ALKALI ANTIMONIDES

Compound	Prep.	Structure Type	Lattice Constants in Angstroms	Method	Photosens. μa/1	Ref.	Quant.* Anal.	Remarks
Li_3Sb	Bulk	DO_3	a=5.559	X	-	i	yes	
Li_3Sb	Bulk	DO_{18}	a=4.701,c=8.309	X	-	i	yes	
Na_3Sb	Bulk	DO_{18}	a=5.355,c=9.496	X	-	i	yes	
Na_3Sb	PC	DO_{18}	a=5.34, c=9.50	ED	0.05-.15	IX,FR	no	
K_3Sb	Bulk	DO_{18}	a=6.025,c=10.693	X	-	i,FR	yes	
K_3Sb	Powder	DO_{18}	a=6.034,c=10.716	X	-	IX,FR	no	
K_3Sb	PC	DO_{18}	a=6.02, c=10.73	X,ED	0.6-2	FR	no	annealed sample, conv. from DO_3
K_3Sb	PC	DO_3	a=8.493	X,ED	2-12	FR	yes	
Rb_3Sb	Bulk	DO_{18}	a=6.283,c=11.18	X	-	ii	yes	
Rb_3Sb	Powder	DO_{18}	a=6.32, c=11.19	X	-	iii	no	
Rb_3Sb	Powder	DO_3	a=8.84	X	-	iii	no	
Rb_3Sb	PC	DO_{18}	(none given)	X	3-5	I,iii	no	annealed sample
Rb_3Sb	PC	DO_3, B32	a=8.89(I)	X	8-13	I	no	
Cs_3Sb	Bulk	DO_3	a=9.184	X	-	ii	yes	
Cs_3Sb	Powder	B32	a=9.147-9.19	X	-	v	yes	
Cs_3Sb	Powder	A2 or DO_3	(none given)	X	-	v	no	
Cs_3Sb	PC	A2 or DO_3	a=9.12	X,ED	10-38	I,vi	no	very broad lines
Cs_3Sb	PC*	B32	a=9.176	X	-	I,vi	no	annealed sample
Cs_3Sb	PC*	DO_3	a=9.180	X	-	I	no	annealed sample
Na_2KSb	Powder	DO_3	a=7.74	X	-	v	yes	
Na_2KSb	Bulk	DO_3	a=7.723	X	-	vii	yes	solid solution to $Na_{1.95}K_{1.05}Sb$

TABLE I - CONTINUED

Compound	Prep.	Structure Type	Lattice Constants in Angstroms	Method	Photosens. μa/1	Ref.	Quant.* Anal.	Remarks
Na_2KSb	PC	DO_3	a=7.72	X,ED	15-40	FR	no	unannealed
Na_2KSb	PC	DO_3	a=7.727	X	-	X	no	annealed samples
$Cs:Na_2KSb$	PC	DO_3	a=7.740	X,Ed	65-110	X	no	unannealed samples
$Cs:Na_2KSb$	PC	DO_3	a=7.743	X	-	X	no	annealed samples
K_2CsSb	Powder	DO_3	a=8.615	X	-	XIII,IX	no	solid solution Cs_3Sb to $K_{2.08}Cs_{0.92}Sb$
K_2CsSb	PC*	DO_3	a=8.615A	X,Ed	55-80	IX	yes*	*on annealed samples

Definitions of abbreviations and symbols:

Prep.: Bulk - Sample prepared at high temperature, usually from a melt.
Powder - Sample prepared below 250° by reacting Sb powder with alkali metal vapor.
PC - Sample prepared as photocathode. Lattice constant data usually obtained by x-rays from sample annealed in capillary unless otherwise noted.
PC* - Indicates annealed sample showing additional super lattice lines.

* Indicates whether or not a quantitative analysis of the intensities was made as opposed to characterization by the types of diffraction lines present and a qualitative indication of their intensity.

References: (Roman numerals refer to reports of this project; FR to this report)

(i) G. Brauer and E. Zintl, Z. Phys. Chem. B37, 323 (1937).

(ii) G. Gnutzmann, F. W. Dorn and W. Klemm, Z. Anorg. u. allgem. Chem. 309, 189 (1961).

(iii) J. Chickawa, S. Imamura, K. Tanaka and M. Shiojuri, J. Phys. Soc. (Japan), 16, 1175 (1961).

(iv) K. Jack and M. Wachtel, Proc. Roy. Soc. (London) 239A, 46 (1957).

(v) J. S. Scheer and P. Zalm, Philips Res. Rept. 14, (1959).

(vi) W. H. McCarroll, J. Appl. Phys. 32, 2051 (1961).

(vii) W. H. McCarroll, J. Phys. Chem. Solids, 16, 30 (1960).

is larger than its hexagonal counterpart (where one exists, the counter parts of the bialkali cathodes are considered to be the hexagonal binaries). (2) When the compound is prepared as a powder or as a bulk sample where polymorphism exists, the hexagonal modification results. In the two cases where the hexagonal and cubic polymorphs exist, it is possible to irreversibly convert the cubic form into the hex form by annealing at 160-180°C for several hours. It thus appears that the cubic form is stabilized when prepared in the form of a thin film. This may be due to the smaller crystallite size of the unannealed and the inevitable strains associated with it. (3) All of the cubic materials, when prepared as photocathodes, appear to be in the structure indicative of the highest degree of order with the possible exception of Cs_3Sb. In the case of the latter, it is extremely difficult to distinguish between a case of complete disorder and one of higher order from an analysis of the Bragg intensities if one has a sample of small crystallite size (I-7).[7] (4) In the case of powdered samples of Cs_3Sb, it has been possible to prepare it in the partially ordered form. This has also been reported for Rb_3Sb also.[8] Similar results have been reported for Cs_3Bi powders but when the material is prepared as a thin film photocathode, the ordered DO_3 structure results.[9]

4. Structure of Cubic K_3Sb

It has been shown by a combination of x-ray and electron diffraction studies that the brown form of K_3Sb has face-centered cubic unit cells with a = 8.49 A. The particular sample chosen for study was a photocathode prepared from a layer of antimony evaporated from PtSb, exposed to a glow discharge in oxygen and further processed by the addition of more Sb followed by K addition.

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[7] W. H. McCarroll, J. App. Phys. 32, 2051(1961).

[8] J. Chikawa, S. Imamura, K. Taraka, and M. Shiojuri, J. Phys. Soc. Japan 16, 1175(1961).

[9] G. Oertel, Am. Phys. 8, 138(1961).

Qualitative examination of the x-ray powder diffraction pattern of the unannealed sample showed that all types of face-centered cubic reflections were present which indicates that the basic structure of the material is derived from the DO_3 structure. However, certain anomalies exist in the intensities which could be explained on the basis of one or two possibilities: (1) A considerable amount of disorder exists such that the true condition of the structure lies somewhere closer to the B32 structure than to the DO_3 type. (2) Because of abnormally large and different amplitudes of vibrations of the various atoms present, it is necessary to apply large Debye-Waller factors to the atomic scattering factors of the atoms which occupy the positions of the DO_3 structure. The use of large temperature factors was necessary in order to explain the data for Cs_3Sb[10] and cubic K_3Bi.[11] Proper analysis of both possibilities would most conveniently and economically be accomplished by use of a computer. Unfortunately, the proper programs were not available in this laboratory, and it would be a matter of a few weeks before one could either be written or obtained from other sources. In the interim, it was decided to do a few calculations by hand since the expiration date of this contract was approaching and since there was a fairly simple calculation that could be made to see if the temperature or Debye factor was applicable. This is based upon the fact that the intensity of the diffraction lines of the type $h+k+\ell = 4n$ will be independent of the degree of order. In addition, the intensity of these diffraction beams result from the full cooperative reenforcement from the scattering amplitudes of the atoms in all positions of the structure. Further, a plot of the difference in the logarithms of the observed and calculated intensity as a function of

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10. K. H. Jack and M. M. Wachtel, Proc. Roy. Soc. A239, 46(1957).
11. D. E. Sands, D. H. Wood, and W. J. Ramsay, Acta Cryst. 16, 316(1963).

the angle of diffraction should yield a straight line regardless of whether all atoms vibrate with equal amplitude. (Isotropic vibration is assumed, however.) The slope of this line is a measure of the Debye-Waller factor. If the amplitude of vibration is different for different atoms or different positions, it will show up as a noticeable deviation from a straight line in a similar plot of those reflections whose intensity depends on the difference betweer the scattering factors of atoms in different positions (i.e., for all $h+k+\ell = 4n+2$). Indeed, this is precisely what is seen from such a plot (see Fig. 9). Using this plot and the deviations from it, an estimate of the temperature factors required was made. After three refinements, the following set of temperature factors were obtained using the criterion of the best over-all fit of the observed and calculated intensities for their selection:

For Sb	$B = 1.5\ A^2$
For K in (c)	$B = 5.5\ A^2$
For K in (b) and (d)	$B = 3.2\ A^2$

The set of calculated data obtained in this fashion is given in Table II. A further least squares refinement of the data is contemplated. The observed data appear to be sufficiently well explained on this basis and it can be stated with confidence that no large departure from order does exist. However, it should be borne in mind that large temperature factors in themselves are somewhat suspect and often compensate for effects other than increased amplitudes of vibration. Among these are the effects of disorder. It might be possible from an analysis of the diffuse background scattering of the diffraction pattern to determine this, but such a study is not planned at present.

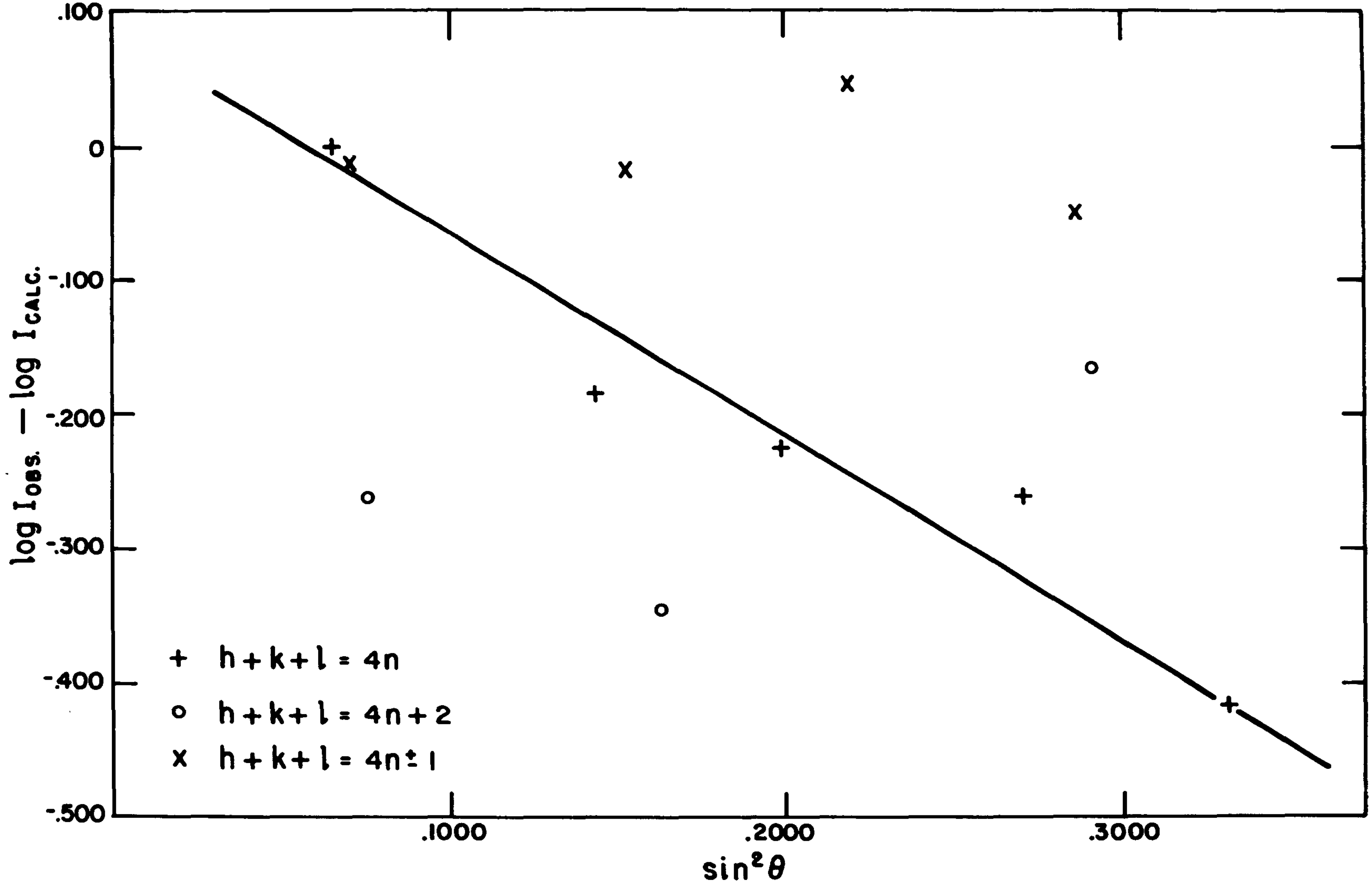
.100
0
-.100
-.200
-.300
-.400
-.500
log I$_{OBS.}$ — log I$_{CALC.}$
.1000
.2000
.3000
sin$^2\theta$
+ h+k+l = 4n
o h+k+l = 4n+2
x h+k+l = 4n±1

FIG. 9

TABLE II

INTERPLANER SPACINGS AND INTENSITY DATA FOR K_3Sb

hkℓ	d_{obs}	a_o	I_{calc}	I_{obs}
111	4.891	8.471	20	28
200	4.255	8.510	11	10
220	2.998	8.479	80	100
311	2.554	8.470	14	13
222	2.453	8.497	3.4	2.5
400	2.122	8.488	12	11
331	1.951	8.504	6.3	6.0
420	1.898	8.488	4.5	2.7
422	1.733	8.490	21	22
511,333	1.638	8.511	4.9	6.1
440	1.495	8.480	5.7	5.9
531	1.437	8.501	4.2	4.1
600,442	1.421	8.526	1.8	2.2
620	1.342	8.488	6.7	5.6

5. Lattice Constant of the S-20 Cathode

A comparison of lattice constants of the S-20 type cathode, Cs:Na_2KSb, and the bialkali cathode, Na_2KSb, was made from the back reflections of the x-ray diffraction patterns of both annealed and unannealed samples. The detailed data are given in (X-29). An average value of $a = 7.7274 \pm 0.0016$ A was obtained for three bialkali cathodes whose sensitivity ranged from 10 to 28 μa/lumen. A significantly larger lattice constant was obtained for the cesiated S-20 cathode. A value of $a = 7.7423 \pm 0.0023$ A was obtained from three cathodes whose sensitivities ranged from 65 to 83 μa/lumen. Attempts to prepare cathodes of higher sensitivities in the scraper tube have not been successful. The change in lattice constant can be explained either as a surface or bulk effect. The annealing of the sample in any event would certainly cause diffusion of any surface cesium into the bulk and thus, in the cases of annealed samples, what is being measured is a bulk effect. On the other hand, the lattice constant obtained from an unannealed sample with sufficiently sharp back reflections was found to have a value essentially the same as those found for annealed samples. It would be most surprising if the surface and bulk effects yield essentially the same lattice constant. In addition, a simple calculation, assuming Vegards law to be valid, leads to the result that as much as a ten to twenty fold excess of cesium could be present over the amount required to form a surface monolayer and that as much as 2 per cent of the alkali metal sites are occupied by cesium. It is recognized that serious deviations from Vegards law are possible at the extrema of solid solution and this must be borne in mind in considering the above figure.

6. Ag-Cs-O Cathode

Structural data for this cathode was obtained using electron diffraction techniques. Although normal processing schedules were followed, it was not possible to prepare a cathode with a response above 10 μa/lumen. Thus, in discussing this work, the assumption is made that the optimum response of a photocathode is not a function of the gross crystal structure. Details of the experimental work are given in (XI-31, XII-43). The phases observed by electron diffraction essentially confirm the composition of the cathode which has been predicted from indirect evidence by other workers, namely, that the cathode is a mixture of Cs_2O and Ag formed by the reduction of a layer of Ag_2O by the addition of cesium. The diffraction patterns of the cathodes were rather poor, but all lines could be accounted for on the basis of the above mixture. However, the presence of other cesium oxides cannot be ruled out (XII-44).

A brief study was also made of the phases which result when the cathode is exposed to an excess of oxygen. Such exposure results in a definite and reproducible change in the pattern, accompanied by a complete loss in photoresponse. The electron diffraction pattern appears to be that of Ag and Cs_2O_3, although the data for the latter are not sufficient to make a final positive identification. Addition of cesium partially restored the photoresponse and regenerated the original diffraction pattern.

7. Ag-Bi-Cs-O Cathode

X-ray diffraction studies using the window tube showed that this cathode is a mixture of Cs_3Bi and Ag (IV-19). No lines for Cs_3Bi of the type $h+k+\ell = 4n+2$ were observed. Such lines are indicative of a higher degree of order but their observation would have been difficult because of the conditions of the experiment. It is possible, however, that the presence of silver does influence the degree of order. On the other hand, it is clear that the introduction of silver into Cs_3Bi does not introduce a gross structural change. The previous report (III-17) that the sensitive phase might be non-cubic was in error, apparently due to a thickness effect caused by the necessity of preparing abnormally thick cathodes in order to obtain a sample for the scraper tube.

8. Crystallite Size Studies

An estimate of the relative crystallite size of photocathode samples was obtained by the measurement of the width of the diffraction lines. The methods and the limitation of the technique are given in (XI-31). One of the purposes of the study was to see if any correlation existed between crystallite size and the absolute value of photoemission. The data given in Table III for several cathodes show no definite relationship between the two. However, the effect of annealing has a definite effect on the crystallite size.

Measurements of this effect are planned on Rb_3Sb and K_3Sb in which the samples are annealed in an excess of alkali vapor while the sample is still in the form of a thin film cathode. This will be useful in confirming the postulate that an increase in crystallite size is necessary to cause conversion from the cubic to the hex form.

TABLE III

CRYSTALLITE SIZE OF ALKALI ANTIMONIDE PHOTOCATHODES

Compound	Unannealed	Annealed
Cs_3Sb	75-83 A (2)	199-211 A (2)
Na_2KSb	113-169 A (4)	255-376 A (2)
$Cs:Na_2KSb$	94-165 A (3)	185-217 A (3)
K_2CsSb	108-113 A (2)	237-259 A (2)

Numbers in parentheses refer to the number of samples examined. The absolute values may be considerably in error. However, they are useful for comparison purposes.

B. Low Energy Electron Diffraction

The original experiments concerning the diffraction of electrons[12] were conducted using slow electrons. Because of the low energies of the electrons involved, their interaction with the solid takes place in the first few atom layers and the diffraction pattern obtained is influenced largely by the nature of the atomic arrangement of the surface. Such a tool obviously would be of great value in studying processes whose mechanisms are strongly influenced by the condition of the surface (e.g., electron emission from solids).

However, most real surfaces are covered by a layer of absorbed gases, or a compound formed by reaction with the ambient, which can be several atom layers thick. This absorbed layer is usually amorphous and no diffraction

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[12] C. J. Davidson and L. H. Germer, Phys. Rev. 30, 705(1927).

pattern is observed with low energy electrons unless the surfaces are somehow cleaned and maintained clean in high vacuum conditions. In early experiments, the collection of data was tedious and time consuming, and there was always the danger that the condition of the surface would change before the experiment was completed. Because of these disadvantages, very little work (with some notable exceptions) was done with low energy electron diffraction until 1960 when the availability of ultra-high vacuum equipment, coupled with a basic improvement in the design of the diffraction apparatus,[13] allowing the pattern to be displayed instantaneously, triggered a virtual renaissance in the field.

Because of the importance of the surface in hot electron and field induced photoemission processes, it appeared that this technique could be used to advantage for the study of such surfaces. Low energy diffraction apparatus was therefore built. However, because of commitments to other aspects of this program, a relatively small proportion of time was devoted to this study.

The initial apparatus (I-6, IV-20) was of the display type described by Germer and co-workers[13] which was based upon the work of Ehrenberg.[14] In this tube, the diffracted electrons were displayed on a flat plate phosphor screen. This tube was used to examine a clean silicon (111) surface (VI-21) and it was found that the heating and annealing process had produced the so-called Si (111)-V surface described by Germer and MacRea.[15] However, it was not possible to obtain diffraction patterns with electrons whose energies were much less than 45 volts.

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[13] E. J. Scheibner, L. H. Germer, and C. D. Hortman, Rev. Sci. Instr. 31, 112(1960).

[14] W. Ehrenberg, Phil. Mag. 18, 878(1934).

[15] L. H. Germer and A. U. MacRea, J. Chem. Phys. 37, 1382(1962).

Because of this, it was decided to modify the tube according to the suggestions of Lander, Morrison and Unterwald[16] who replace the flat plate grid and phosphor screen with one of spherical design which allows operation without serious distortion at much lower voltages. This revision was incorporated only recently, and the single experiment performed with it is described below.

A crystal of silicon initially believed to have been cut so as to expose the (111) surface was optically polished and etched with iodine etch before insertion in the tube. Subsequent experiments showed that this surface was actually a slightly misoriented (211) surface. After bakeout of the tube at 200°C, the crystal was heated to 1230°C for several minutes. This yielded a spot pattern on cooling which might be expected from a misoriented (211) surface. Patterns were observed from 8 to 200 volts. (The fact that the (211) surface was present was later confirmed by x-ray diffraction.) However, because of the misorientation, a more detailed interpretation of the pattern was not attempted. Rather, the nature of the changes in it were noted as a function of the processing.

The ambient pressure when the crystal was cool was between $7\text{x}10^{-10}$ and $1\text{x}10^{-9}$ Torr. On standing for several hours, the intensity of the diffraction pattern diminished and only the stronger spots were visible. A 10-second flash of the crystal at 1000°C was sufficient to regenerate the original pattern. This was followed by a controlled deposition of Cs using an atomic beam of the type developed under this project for the molecular beam deposition of photocathodes. The control of the beam was checked by monitoring the photoemission, with monolayer converage taken to correspond to the maximum in the

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[16] J. J. Lander, J. Morrison, and F. Unterwald, Rev. Sci. Instr. 33, 782(1962).

photoelectric current. The effect of the Cs deposition was to slowly diminish the intensity of the diffraction pattern without introducing any new superstructure. This was interpreted as meaning that Cs deposits on the surface in a disordered fashion. Low temperature annealing did not induce order while flashing the crystal at 1000°C regenerated the original surface pattern.

It thus appears that Cs cannot be ordered on Si (211) under the conditions of this experiment. It is possible, however, that ordering could be induced if a lower ambient pressure was achieved since at the pressures of this particular experiment, a surface contaminant overlayer of fractional coverage is still a definite probability. Future experiments are contemplated using other orientations and better background conditions.

V. FIELD INDUCED PHOTOEMISSION

A. Introduction

A field induced photoemitter utilizes an internal electric field in the emitter to provide the energy which a conduction band electron must have in order to be emitted into vacuum. In such an emitter, an incident photon must then supply only that energy required to excite an electron into the conduction band. The photothreshold for a field induced photoemitter is equal to the semiconductor bandgap rather than the band gap plus electron affinity as in the conventional photoemitter. Therefore, response is possible to radiation which is further in the infrared with a field induced photoemitter than is possible with conventional photoemitters. During this contract, part of our effort was directed toward attempting to develop a germanium field induced photoemitter.

A convenient way to generate an electric field in a semiconductor is by means of a reverse biased p-n junction. The depletion region between the p- and n-regions act like a thin high resistance region across which a voltage can be applied. Electrons are excited in the p-region by radiation. Upon drifting to the p-n junction, they are accelerated to high kinetic energy. In order to be emitted, the electrons must pass through the depletion region and the n-layer without losing so much energy that they cannot escape over the potential barrier which exists at the semiconductor surface. Because the energetic electrons have a relatively short mean free path between energy loss collisions, the p-n junction must be very close to the semiconductor surface so that the electrons need not travel through a large thickness of material after they have attained high kinetic energy.

The principal problem which must be solved in order to produce a field induced photoemitter is to develop a method of making p-n junctions with extremely thin n-type surface layers. A method must also be found for producing a clean surface on crystals containing p-n junctions on which cesium can be deposited to reduce the electron affinity.

B. Preparation of P-N Junctions

The requirements on the p-n junctions for field induced photoemitters are (1) the dark reverse current must be low so that voltage can be applied across the junction without appreciable heating of the junction region and (2) the junction must be placed as close to the surface as possible so that electrons do not lose appreciable energy in moving to the surface. Together, these conditions are more severe than usually encountered in commercial transistor fabrication since the proximity of a surface usually seems to effect adversely the reverse bias characteristics of a junction. In this case, the junction must be much closer to the surface than in commercial transistors. Our initial goal was to make the junctions approximately 1000 A from the surface, but it is evident that this is just a starting point and that thinner n-regions are required if efficient photoemission is to be achieved.

To minimize the effect of surface leakage where the junction intersects the surface and to provide a region where contact could be made to the thin n-region, a thick annular n-type region was usually diffused into the p-type wafer. The thin n-region from which emission was to be obtained was then prepared within the ring. The diffusion profile of the thick n-region was such that it had a higher reverse breakdown voltage than the thin n-region and therefore did not short out the thin n-region. Generally, it was easy to obtain thick n-regions with good reverse bias characteristics.

The first experiments on diffusion utilized the modified box or powder technique of Gregg and Veloric in which Ge crystals are immersed in arsenic doped Ge powder (I-5). The box was then heated in a hydrogen atmosphere. The diffusion constant for this process was determined as a function of temperature (III-13). The results of these diffusions were junctions with poor reverse characteristics. This problem was ultimately related to the presence of copper impurities in the arsenic doped powder. It was found that a long annealing at 500°C reduced the effect of this impurity, but the junctions were still not very good. It was shown that the poor characteristic was not the result of surface leakage (V-31) but was caused by small scale defects in the thin diffused region. This was shown by dividing a large area diffused region into small areas .020"x.020" and measuring the characteristics of each. No regions were found that had better i-v characteristics than the large area junctions when the difference in area was taken into account (V-32).

As a result of this experiment, a second diffusion technique was tried. In this case, elemental phosphorus was used as the source of doping impurities. The junction was, as before, imbedded in Ge powder but, in this case, pure powder could be used (VI-23). Phosphorus diffusion had an additional advantage that the diffusion constant was lower and therefore the diffusion time for formation of thin junctions was longer. This was helpful because the time necessary for thin diffusion was comparable to the time necessary to heat the apparatus to the diffusion temperature and was therefore difficult to control.

Although this technique required extreme cleanliness (VIII-26), with care, thin junctions could be made which had reverse characteristics comparable to those obtained with thick junctions.

At this time, measurements of field induced photoemission from silicon which will be described below and experience with attempts to produce a clean surface on silicon and germanium crystals containing thin n-regions showed clearly that it is necessary to integrate into the diffusion process a technique for preparing a clean semiconductor surface. This realization, along with the development of vapor transport and vacuum diffusion techniques in the transistor industry in general and in RCA in particular, lead to the development of a third method of preparing p-n junctions for field induced photoemission.

In this method, diffusion was carried out by means of phosphine gas (PH_3) which decomposed at the semiconductor surface giving up phosphorus which then diffused into the semiconductor. Prior to admitting phosphine, the crystal surface could be cleaned with HCl vapor which produced volatile $GeCl_2$ when reacted with hot Ge and left a clean highly polished semiconductor surface. As a final step, the doping gas could be pumped out of the system, leaving a clean semiconductor surface in vacuum (X-37).

Upon completion of the apparatus for vapor etching and diffusion (XI-38), experiments were undertaken which indicate that very good thin junctions could be produced by this technique (XII-56). Although very thin junctions have not yet been made by this method, the results are promising and further efforts in the area of fabrication of thin junctions for field induced photoemission can probably be profitably made along these lines.

C. Measurements on Thin Junctions

In addition to the measurements of the reverse characteristics, measurements have been made of light emission and attempts have been made to measure photoemission, hot electron emission, and field induced photoemission from Ge. Measurements were also made on a silicon p-n junction which was prepared under a contract with USAELRDL, Fort Monmouth, New Jersey.

Measurements of light emission are useful since it has been shown with silicon that a direct correlation exists between light and electron emission. Light emission from germanium is difficult to observe because it is primarily in the infrared. However, by use of a lead sulfide image tube or by careful dark adaption, light emission could be seen from some of the arsenic doped germanium crystals (II-16, III-16, IV-25). The best of these observations showed that light came primarily from discrete spots indicating that the junctions were breaking down non-uniformly. Occasionally, a diffuse glow could be seen especially in the vicinity of the contacts. The small amount of visible radiation precluded the possibility of recording these patterns photographically.

Several attempts were made to observe hot electron emission and field induced photoemission from germanium p-n junctions prepared by diffusion of arsenic or elemental phosphorus. Photoemission from the junctions was measured during the cesium deposition.

In one case (IV-29), hot electron emission of $5x10^{-9}$ amps was observed. By imaging the source of electrons on a phosphor screen, it was seen that the emission came from a thin region where the thick and thin n-type regions joined. An attempt to see field induced photoemission was not successful because the crystal heated excessively when reverse voltage was applied.

Several other attempts to see electron emission were thwarted by either bad contacts (V-32) or broken crystals (IX-33). In these cases, photoemission measurements indicated that the germanium surfaces were not sufficiently clean to yield the minimum electron affinity which is desirable to obtain electron emission. In one case, the photoemission as a function of cesium coverage behaved in a manner similar to that previously observed for contaminated silicon. In the second case, after cesium deposition, a photothreshold of 1.8 ev was measured as compared to 1.5 ev observed with Cs on a clean surface.

Field induced photoemission was observed from a silicon crystal in which a p-n junction had been diffused (X-34 to 37). This crystal was prepared under Contract DA36-039 AMC-02221(E) with USAELRDL, Fort Monmouth, New Jersey. This crystal was cleaned only by etching prior to insertion into vacuum and subsequently did not have an optimum surface. The photothreshold for this crystal after cesium treatment was 2.4 ev compared to 1.5 ev for a clean cesium-treated Si surface. The threshold for field induced photoemission was 1.1 ev, the band gap energy of silicon. From the spectral dependence of the field induced photoemission, the junction depth was estimated to be about 6000 A below the semiconductor surface. The quantum efficiency for field induced photoemission was only $\sim 10^{-7}$. This low response was attributed to the high electron affinity, the excessive depth of the junction below the surface, and attenuation of electrons in the oxide layer at the silicon surface. It was estimated that if these difficulties could be corrected, then efficiencies of at least 0.1% should be possible.

D. Conclusions

It is concluded from this work that the principal problem remains that of fabricating p-n junctions with good reverse characteristics and clean surfaces. By use of vapor diffusion and epitaxial growth, it should be possible to make more progress along these lines than has been made previously. This technique, by which both a junction with a good reverse characteristic and a clean surface can be made, should be the basis for future work in this area.

VI. CONCLUSIONS

(1) By using a thicker initial Sb film, the red response of an S-20 cathode can be increased by a factor of two in those cases where blue response is not important.

(2) A process for producing normal Na_2KSb cathodes with a single Sb film has been developed. Additional Sb is required to make an S-20 ($Cs:Na_2KSb$) cathode.

(3) Only low sensitivity S-20 cathodes could be formed by processing at 160°C instead of 220°C.

(4) The Sb-K-Cs cathode which is characterized by high blue response and low dark current has been developed.

(5) Experiments suggest that the average sensitivity of cathodes made on oxidized Sb is higher than those made without oxidation.

(6) Replacement or addition of Rb, Bi, Ag, B, Pb, Te, and O in S-20 cathodes yielded no improvement in red response or sensitivity.

(7) Differences were observed between the properties of Sb films evaporated from elemental Sb or PtSb alloy. However, no difference was observed on the sensitivity of S-20 cathodes made from either material provided the same number of Sb atoms were used.

(8) Two phases of K_3Sb have been observed which have different crystal structures, optical absorption, and photoemissive response.

(9) Monoalkali antimonide cathodes which have normal sensitivities have been produced by deposition from molecular beams on room temperature substrates.

(10) Multi-alkali antimonide cathodes with normal sensitvities could not be produced by sequential deposition from molecular beams. This result was attributed to the inability to produce a uniform single phase multi-alkali antimonide phase by sequential deposition.

(11) Progress has been made in the development of greatly improved apparatus for the formation of cathodes by simultaneous deposition from molecular beams.

(12) Preliminary experiments have been conducted on cathode formation by use of alkali ions emitted from zeolites.

(13) Structural data have been obtained for all of the normal valent alkali antimonides. Where polymorphic forms exist, the cubic form is always found to be the more photosensitive.

(14) New alkali antimonide phases discovered during the period of this report include K_3Sb and Rb_3Sb with the ordered cubic DO_3 structure and K_2CsSb with the cubic $L2_1$ structure.

(15) The Ag-Cs-O cathode was shown to consist of a mixture of silver and Cs_2O.

(16) The Ag-Bi-Cs-O cathode was found to be a mixture of Ag and Cs_3Bi.

(17) Crystallite size determination revealed no obvious relationship between this property and photoemission.

(18) Vapor etching and diffusion methods have been evolved which appear promising for making thin junctions for field induced photoemission.

VII. RECOMMENDATIONS FOR FUTURE WORK

Despite the extensive investigation which has been carried out, the factors which contribute to and control the red response of photocathodes have not been identified. It is recommended that future work be conducted to study the physical properties of S-20 photocathodes including the band structure, electrical properties, and crystal structure. It is recommended that research be continued on process modifications and substitution of cathode constituents as well as study of other members of the alkali antimonide family since this approach has been most successful in the past.

Experiments should be continued on the deposition of cathodes by simultaneous deposition from molecular beams. This approach continues to offer considerable promise for cathode processing as well as for the study of the photocathode systems. By use of the techniques developed under this contract, it should be possible to fully exploit simultaneous deposition from molecular beams for photocathode fabrication.

Further work should be performed to more fully evaluate the possibilities of producing photocathodes by use of ions from ion emitters.

It is recommended that future work on the preparation of p-n junctions for field induced photoemission be based on the use of vapor diffusion and vapor deposition techniques. Since by use of these methods a clean surface can be produced as well as a shallow junction, progress in the investigation of field induced photoemission should be possible.

Man-hours expended for the period 1 January - 31 March 1965:

	Hours:
Administration	
G. A. Morton	15-1/2
Members of Technical Staff	
C. R. Fuselier	154
W. H. McCarroll	255-3/4
R. E. Simon	201-1/2
A. H. Sommer	193-3/4
Technicians	
G. O. Fowler	232-1/2
R. L. Rodgers	255-3/4
TOTAL MAN-HOURS -	1208-3/4

Ad ______________________

RCA Laboratories, Princeton, N.J.
RESEARCH STUDIES FOR INCREASING THE SENSITIVITY OF PHOTOEMITTERS, Research by R. E. Simon,
A. H. Sommer, W. H. McCarroll and C. R. Fuselier
Final Report for 29 December 1961 to 31 March 1965
74 pages incl. ilus.
(Contract DA44-009 ENG-4913)

A summary of the work performed during this contract is presented. This includes a study of variations in processing and composition of S-20 cathodes and the investigation of antimony films deposited from Sb and PtSb beads. Two different phases of K_3Sb are described. Formation of photocathodes by sequential and simultaneous deposition from molecular beams of the constituents has been examined. The crystal structure of alkali antimonides and other photocathode systems has been studied by means of x-ray and electron diffraction. Attempts to produce shallow p-n junctions in germanium for field induced photoemission are described.

UNCLASSIFIED

1. Study of S-20 photocathode parameters
2. Molecular beam formation of photocathodes
3. Structure studies
4. Field induced photoemission

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II. R.E. Simon, A.H. Sommer, W.H. McCarroll, C.R. Fuselier
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