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A STUDY OF CdS THIN-FILM VACUUM-ANALOG TRIODES

by

Anthony A. Aponick

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Electronic Systems Laboratory
Department of Electrical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

ABSTRACT

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Previous investigations of thin-film gold structures on CdS have shown that gridlike structures with 40-50 percent open area, and sheet resistance 12-50 Ω/sq. can easily be fabricated.

An investigation is made of the possibility of incorporating these structures into active vacuum-analog devices. Solutions to two of the basic problems in achieving this goal are presented and discussed.

The first of these problems, that of insulating the grid structure from the CdS in which it is imbedded, is solved by using aluminum grid material and insulating it with a combination of blocking contact and oxide insulating layer.

The second of these problems, that of achieving a nonlinear conduction law in essentially ohmic polycrystalline CdS, is solved by employing an emitter which makes blocking contact to the CdS. The grid is then used to "pull" electrons over the barrier thus induced in front of the emitter.

The characteristics of such a device which operates in the expected way, but which produces less than unit gain, are presented

Author

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I. INTRODUCTION

This report is concerned with an investigation of the possibility of fabricating thin-film vacuum analog active devices using only simple vacuum deposition techniques. It represents a continuation of the work reported in Electronic Systems Laboratory Reports ESL-R-229, AN ELECTRON MICROSCOPIC INVESTIGATION OF CdS THIN-FILM SURFACES, and ESL-R-237, AN INVESTIGATION OF THIN-FILM GOLD STRUCTURES ON CdS.

The first of these reports was concerned with the crystallinity of CdS thin-film surfaces and their nucleation properties for extremely thin (2.7 to 8.2 $\mu g/cm^2$) deposits of gold. It was found that there existed an intricate balance between substrate temperature and deposition rate, and that the crystallite size and surface asperity was extremely sensitive to the deposition rate. It was learned that depositions onto room temperature substrates at high rates produced nearly amorphous material, while at higher substrate temperatures and lower rates of deposition, crystallites were larger and surface asperities were diminished. The various surface structures were grouped into four basic types. It was also learned that even low surface mass densities of deposited gold formed completely continuous solid-layer structures at room substrate temperatures, while the same surface mass densities formed completely discontinuous agglomerated structures at elevated substrate temperatures. The electron micr-scopic techniques used in discovering these facts are described in detail in both of the previous reports.

The second of these reports was concerned with a more detailed examination of structural formation properties of gold on the various CdS surface types. It was found that gold surface mass densities up to 30 $\mu g/cm^2$ could be forced into the completely discontinuous agglomerated structure. The possible mechanisms for this phenomenon were discussed in some detail, and it emerged that a gas of gold atoms in phase equilibrium with the structural gold could explain all of the observations. This led to the discovery of a method of fabricating thin-film grid-like structures. A thin solid-layer structure was deposited onto a room temperature substrate, and then annealed at high temperature until the emitted gold gas formed holes in the layer. These grid-like structures were catalogued for a wide range of surface mass densities and annealing times with respect to their aperture size and their fraction of open area.

Having developedthe techniques of grid fabrication, the next step was to incorporate the grid into a device. In order to accomplish this, two basic problems had to be solved. In the proposed device, as shown in Fig. 1, the grid is sandwiched between two layers of CdS. It was desired that the flow of electrons be only from electrode No. 1 to electrode No. 3 for all grid voltages.

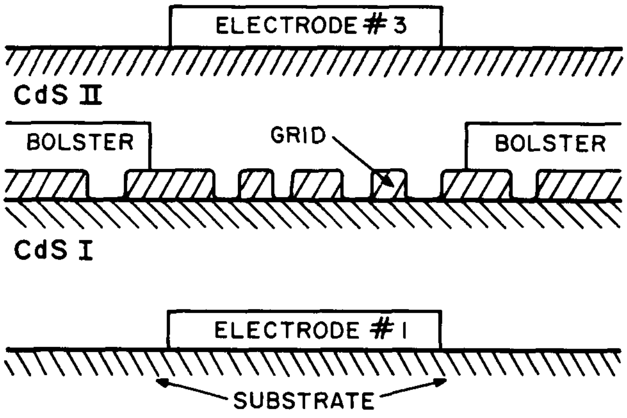

Fig. 1 Schematic Cross-section of a Typical Triode

This would be impossible unless the grid were well insulated from the surrounding CdS. If it were not insulated, it would inject or absorb electrons from the CdS just as easily as the other electrodes.

The problem of grid insulation was solved in two stages. Since, in normal operation, the grid potential was to be negative, the grid could be insulated from the first CdS layer by making the grid-CdS I contact a blocking one. This is equivalent to making the grid-to-electrode No. 1 "diode" back-biased for negative grid voltages. Since no electrons can be injected under these conditions, the grid is effectively insulated from CdS I.

Insulating the grid from CdS II was more difficult. Diodes in which the first electrode deposited makes the blocking contact can not be repeatably fabricated. This problem was finally solved by actually insulating the grid structure with an oxide layer, produced by chemical reaction with the grid material. This, of course, could not be accomplished with gold grids. The only grid material found which could be successfully insulated was aluminum. Unfortunately, it was found difficult to form a well-developed grid structure with this material.

The second basic problem which had to be solved concerned the essentially ohmic nature of thin-film CdS. In single crystal CdS, the conduction process has been found to be space-charge-limited, analogously with the vacuum case. Unfortunately, the conduction law for the untreated polycrystalline films used in this investigation was most often linear. It was found, however, that blocking contacts could repeatably be induced by treating the surface of a CdS deposition with an oxygen glow discharge. A blocking contact causes the conduction law to be nonlinear, and this nonlinearity can be effectively incorporated into the device. The surface of CdS II was treated with the discharge before applying electrode No. 3. Electrode No. 3 was then used as the emitting electrode, and the desired nonlinearity was introduced "behind" the grid. The flow of electrons from electrode No. 3 (the emitter) to electrode No. 1 (the collector), can then be usefully modulated by the grid.

It should be noted that the ohmic electrode No. 1 was originally intended to serve as the emitter, and all of the early devices of this investigation were fabricated with this in mind. Such devices were to operate in strict analogy with a vacuum triode. The considerations discussed above forced abandonment of this idea and the later devices were constructed with electrode No. 3 serving as a blocking emitter. These are called "enhancement" triodes because when electrode No. 1 is at a positive potential with respect to electrode No. 3, the blocking contact is back-biased and almost no current flows until the grid potential is made positive. These devices actually work, but due to the high grid voltages required for modulation, exhibited less than unit gain. The most probable reason for the requirment of high grid voltages is the presence of too much insulation in the holes of the grid. This insulation is in turn probably due to the small size of the apertures in the grid. If the apertures in the grid could be made larger, insulating the grid material would be less likely to cause a build up of insulating material in the holes. It is not inconceivable that a thorough investigation of the formation properties of aluminum grids, and the factors inhibiting the formation process, could permit fabrication of excellent devices using only the techniques described in this report.

II. TRIODE FABRICATION

The devices investigated in this study were all of the same general construction. As shown in Figs. 1 and 2, a grid-like structure was sandwiched between two layers of CdS which in turn was contacted by means of two conducting layers of gold. The proposed principle of operation was based on the following assumptions:

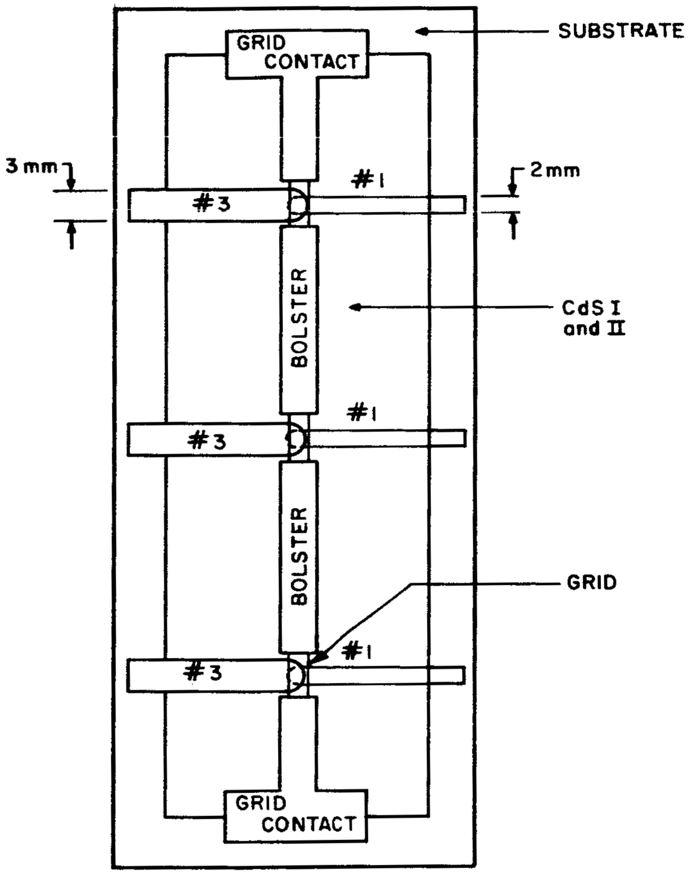

Fig. 2 Arrangement of Electrodes on Substrate

1. The bottom electrode (No. 1 in Fig. 1) will inevitably make ohmic contact to the CdS. Hence, it can be used as an emitter analogously with the cathode in a vacuum triode.
2. The conduction process between electrodes No. 1 and No. 3 is space-charge limited.

3. The grid electrode, if sufficiently insulated from the surrounding CdS, can be used to alter the potential distribution between electrodes No. 1 and No. 3, and hence modulate the flow of space-charge-limited current.

It was discovered in the course of this work that the assumption of space-charge-limited current was unfounded. The reasoning which led to this discovery and a suggestion for a possible solution are discussed in section V-B.

It was found that the most difficult problem in the fabrication of these devices was that of insulating the grid. If the device is used analogously with a vacuum triode, voltage excursions of the grid would be negative with respect to the grounded emitter (electrode No. 1), while the collector (electrode No. 3) would be at a positive dc voltage. Hence, the grid is likely to leak electrons to the emitter and the collector since it is at a negative potential with respect to both. The solution of this problem is discussed in ensuing sections.

The procedure used to fabricate the devices was as follows:

1. Deposition of Electrode No. 1

   400 Å of gold was rapidly evaporated onto a substrate at room temperature. This electrode was a solid layer of gold, and was expected to retain its integrity throughout all of the thermal cycling necessary to produce the grid.

2. Deposition of First CdS Layer

   The substrate temperature was ~ 100°C., equilibrated for 1 hour. The source was degassed 10 minutes at 800°C., then evaporated at 885°C. for 1 hour. These conditions produce a Type III surface of great smoothness and crystallinity.[1] The thickness of the resultant coating was 4800 Å.

3. Surface Treatment for Grid Insulation

   This process was thoroughly investigated and is described in Section III.

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[1] ESL-R-229, Pg. 15

4. Deposition of Grid Contact

   400 Å of gold was rapidly evaporated onto the CdS coated substrate at room temperature as shown in Fig. 2. This electrode also maintained its integrity during grid formation.

5. Grid Deposition

   A source of 27.5 mg. (15 $\mu g/cm^2$) of gold was deposited as shown in Fig. 2 onto the room temperature substrate. In later work it was found feasible to use the same nominal deposition thickness of silver and even aluminum for the grid electrode.

6. Grid Formation

   The temperature of the substrate was raised as quickly as possible to 425°C. and held at this temperature for about 15 minutes, exactly as described in ESL-R-237. This process produced the grid-like structure shown in Fig. 19 of that report. While the sheet resistance of this structure was only of order 50 Ω/sq. the resistance of the configuration shown was 700 Ω. In order to reduce this, the "bolster" material was applied as shown in Fig. 1.

7. Grid-Electrode No. 3 Insulation

   The processes used for this step were thoroughly investigated and are discussed in Section IV.

8. Deposition of Second CdS Layer

   This step was identical with step 2. In some instances, two sources were applied in sequence to make the grid to electrode No. 3 distance twice that from the grid to electrode No. 1. Presumably, this would optimize the modulation factor of the device if electrode No. 1 were used as the emitter.

9. Deposition of Electrode No. 3

   400 Å of gold was rapidly evaporated onto the room temperature substrate as shown in Fig. 2.

III. THE GRID-ELECTRODE NO. 1 CONTACT

In device operation the grid potential was always to be negative with respect to electrode No. 1. Hence, it was assumed that a blocking contact made by the grid to the CdS would suffice to stop injection of electrons from the grid to electrode No. 1. It has been found in previous work that an electrode deposited on the top of a CdS deposition can, and often does, make blocking contact.[2] A method was discovered of treating the CdS surface before applying the grid material which always produces excellent grid-electrode No. 1 "diodes" in which the grid makes blocking contact. The CdS surface was exposed to a 100 micron Hg oxygen glow discharge for 1 hour. The substrate was held at a temperature of 150°C. The discharge was formed between a circular aluminum "cathode" ring and the metallic substrate support. The plane of the ring was 3 cm. from the treated surface, but no part of the substrate was directly over the ring. Both 1500 volts dc (with the ring negative) and 2000 volts rms ac appear to give equally good results. After discharge, the vacuum was restored to the bell jar of the evaporator and the substrate was heated to 325°C. for 1 hour. After cooling to room temperature, the grid material was deposited and formed. A typical v-i characteristic[3] for the diode formed between the grid and electrode No. 1 is shown in Fig. 3. This procedure was followed many times, and no failures and only slight deviations from Fig. 3 were noted. Observe that as long as the grid potential is negative with respect to electrode No. 1, it is essentially insulated.

An electron microscopic check was made to ascertain if the grid formation parameters were different on this surface. Five separate grid electrodes were placed on a discharge-treated CdS surface above a common bottom electrode. A region of the CdS which was to be

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[2] R.E. McAfee, "Current Flow in a Thin-Film Cadmium Sulfide Diode", M.I.T., M.S. Thesis, 1963.

[3] These characteristics are called "heterojunctions" because of the combined effects of rectification and insulation.

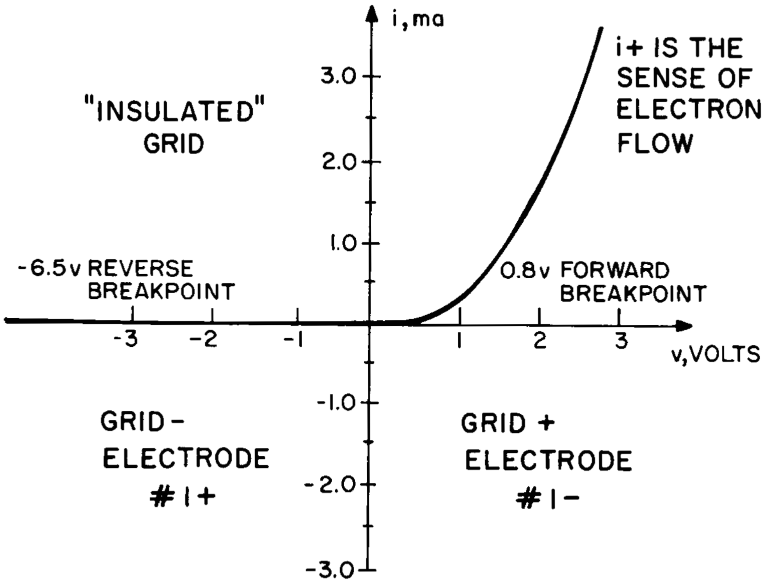


Fig. 3 The V-I Characteristic for the Grid-To-Electrode No. 1 Contact

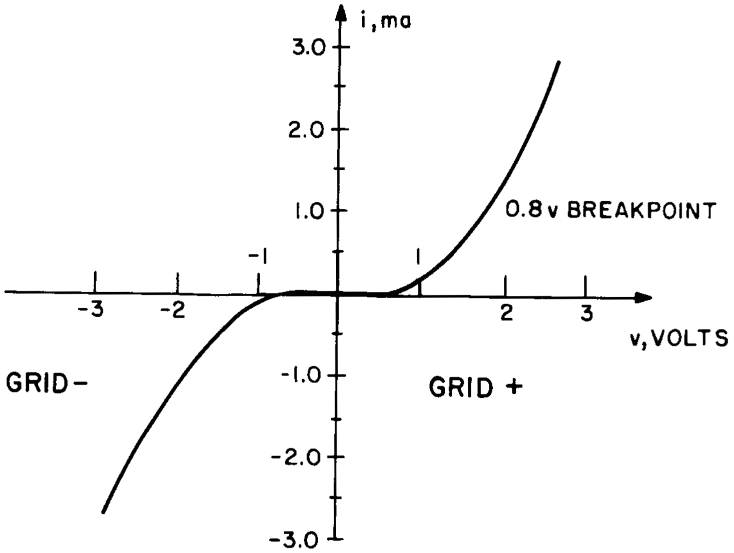


Fig. 4 The V-I Characteristic for Insulating Layer Contact

occupied by two of the grids was deliberately masked from direct access to the discharge. After grid formation with v-i characteristics of these two diodes were of the insulating layer type shown in Fig. 4. The other three were as in Fig. 3. The formed grid sheet resistance averaged 25 Ω/sq. after only 5 minutes of annealing at 425°C. It was felt that grid formation is in some sense "easier" on these treated surfaces, and this was borne out by the electron micrographs. Fig. 5 shows a combination replica of one of the blocking contact grids, and Fig. 6 shows an insulating layer grid. Note that their structure is essentially identical and that, for these formation parameters, their fraction of open area is much larger than their counterparts in ESL-R-237.

Replicas of the CdS surface in the two areas were also examined. Fig. 7 shows the surface and some residual material left imbedded in the carbon after disolving the CdS in HCl. Fig. 8 shows a diffraction pattern produced by this residue. It is not known what this material is, but it evidently plays a role in forming the blocking contact. Fig. 9 shows a replica from the masked-off area of the sample. Note that while the surface of Fig. 7 is amost entirely covered with residue, Fig. 9 seems to show very little. Assumedly, the layer of this residue is formed by the oxygen discharge. The diffraction pattern of this substance is distinctly different from those notes in ESL-R-229. It might be argued that the diffraction pattern observed here is one containing little c-axis component diffractions instead of just the planar hexagons noted in ESL-R-229. If this were so, the (100) spacing should show up in one of the rectangular directions. This is unfortunately not the case. The two spacings noted in the pattern of Fig. 8 are 6.15 Å and 5.71 Å, entirely too large for the (100) spacing of 4.53 Å so extensively measured in ESL-R-229. It can only be assumed that the material seen here is different from the insoluble residue formed on untreated CdS surfaces.

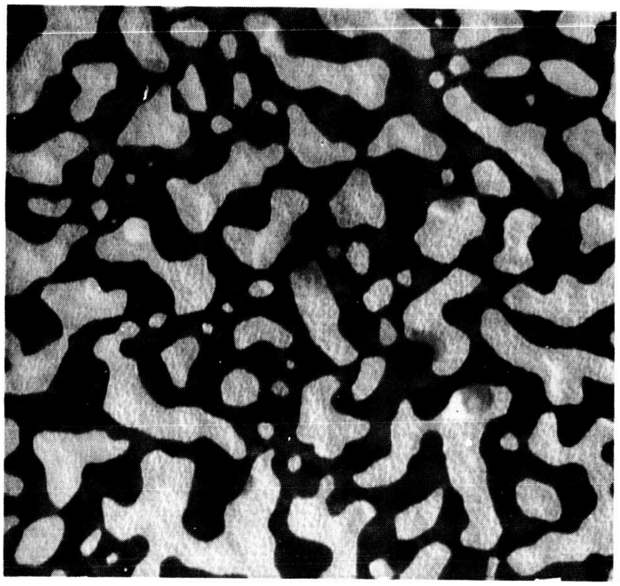


Fig. 5 Grid Formed on Treated CdS Combination Replica, 80,000 x

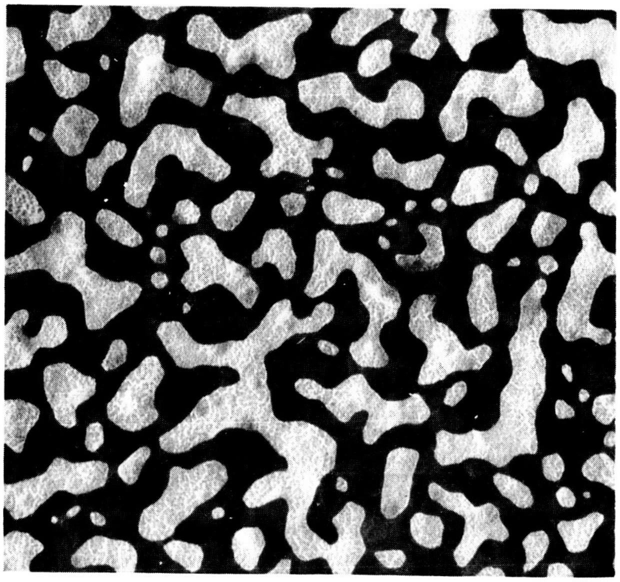


Fig. 6 Grid Formed on Masked CdS Combination Replica, 80,000 x

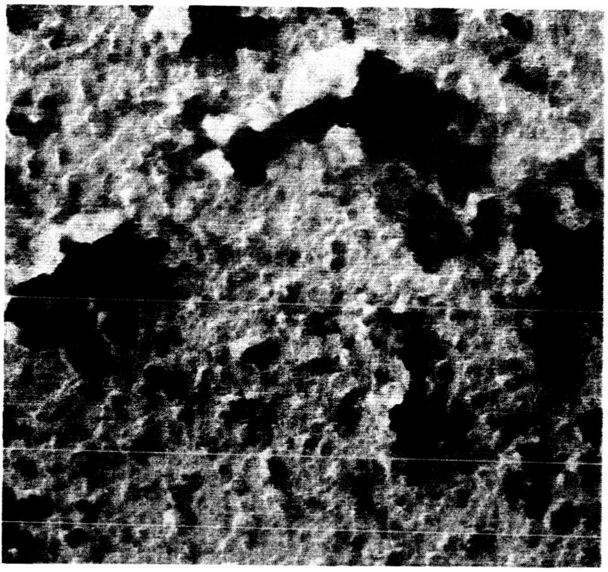


Fig. 7 Residual Material on Treated Surface. Combination Replica, 80,000 x

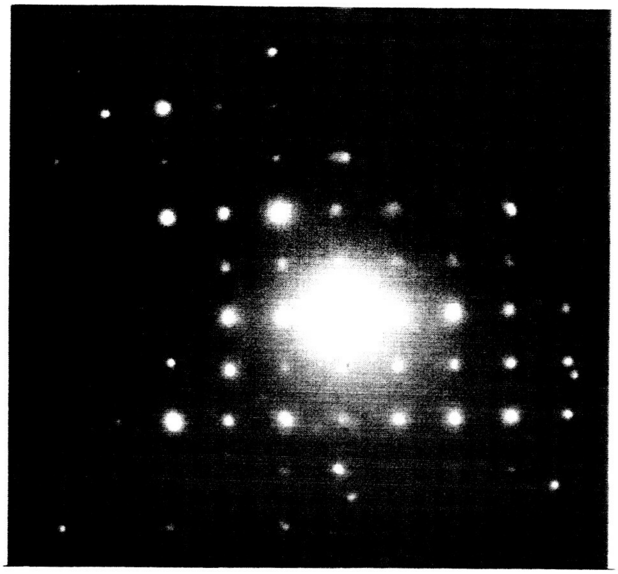


Fig. 8 Diffraction Pattern of the Residual Material of Fig. 7

Fig. 9 Residual Material on Masked Surface. Combination Replica, 80,000 x

IV THE GRID-ELECTRODE NO. 3 INSULATED CONTACT

As was mentioned above, diodes for which the electrode nearest the substrate makes the blocking contact have only rarely been found. The reason for this might be that, as pointed out in ESL-R-229, the upper-surface material in a CdS deposit from an exhaustible molybdenum boat is more crystalline and thus more like single-crystal CdS. An electrode of a metal with the proper work function can make a blocking contact to this material, while any electrode always makes ohmic contact to the nearly amorphous, initially deposited CdS. In order to insulate a grid electrode from a subsequent deposition of CdS, the idea of making the grid a blocking electrode in a diode must be abandoned. In addition, the idea of depositing a thin layer of a good insulator such as SiO_2 immediately over the grid, and then the CdS, is not correct. Any insulation of the grid provided by this method insulates the holes in the grid equally well. When sufficient potential is applied to electrode No. 3 to draw electrons through the holes in the grid from electrode No. 1, the current could just as easily come from the grid electrode itself.

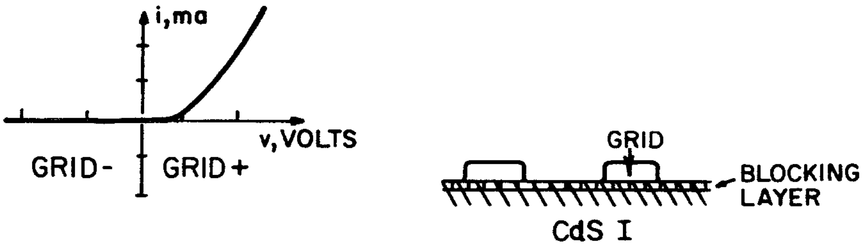
It is seen that what was needed was a means of selectively insulating the grid metal without affecting the holes. Unfortunately, gold is too noble a metal to lend itself well to any such procedure. For this reason, grids of silver were studied.

The solubility of silver in HCl prevented any electron microscopic examination of formed grids. It was found, however, that the electrical resistance of the deposit during the formation process followed identically the pattern of gold grid formation: first, a decrease to approximately 2/3 of the initial resistance of the layer as the applied heat removed dislocations and enlarged crystallite size, followed by an increase in resistance which continued throughout the remainder of the heating cycle. This was considered to be enough indication that a grid-like structure had indeed been formed. This assumption was strengthened by later observations, described below

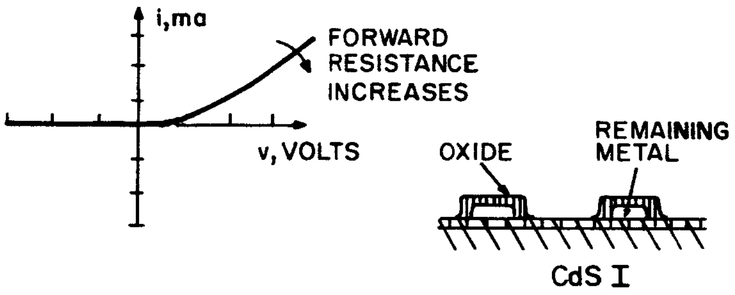
Two means of selectively insulating this structure from the subsequent deposition of CdS were tried. First, oxidation of the silver metal with an oxygen glow discharge and, second, forming a layer of Ag_2S on the grid by exposing it to an atmosphere of hot H_2S. The first of these processes was done in the evaporator using the same cathode ring arrangement described for CdS surface treatments. The substrate was heated to 150°C, and a 1500 volt dc discharge was allowed to proceed for 1 hour. The resistance of the grid structure was monitored during deposition and was found to increase throughout the discharge process. The results of this method are shown in Fig. 10. It is seen that the grid-electrode No. 1 diode serves as an excellent indicator of the condition of the grid and its insulating layer. After forming the grid, but before applying the insulation, the v-i characteristic appears as in Fig. 10(a), essentially the same as for the gold diodes discussed above. As the metal is oxidized, the forward resistance constantly increases as shown in Fig. 10(b). Finally, after the second layer of CdS is deposited, the characteristic appears as in Fig. 10(c). The reverse resistance of the diode which has been established on the lower face of the grid has become shunted by the relatively low resistance paths in the holes as shown. While this is an extremely undesirable effect, it is positive indication of the presence of holes in the grid structure. When the third electrode is deposited, the characteristic is, as expected, essentially the same as that shown in Fig. 10(c), but the breakpoints are lower. The insulation applied to the grid is insufficient for reasonable device operating voltages.

The treatment of the silver with hot atmospheres of H_2S at various pressures produced even poorer insulation. The principal problem with these techniques seems to be that once reaction is initiated, the surface of the grid material does not become passivated against further attack by the reagent. This is probably because of the solubility of oxygen and H_2S in the silver. The reagent dissolves in the grid material, and reacts in the bulk as well as on the surface, eventually destroying the entire electrode. This was observed several times.

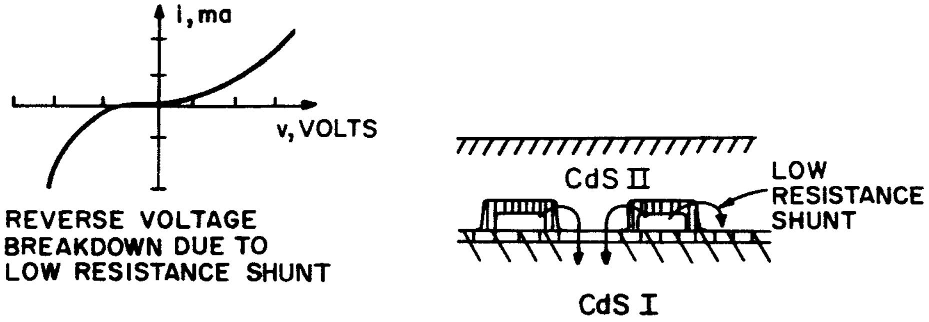
The next step in the investigation was to try an aluminum grid electrode. Surprisingly enough, when the first CdS surface was treated as described above, aluminum electrodes were found to make excellent



a) After grid formation

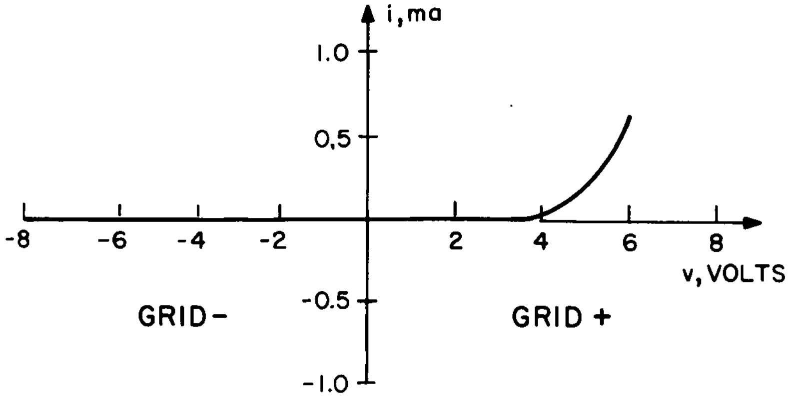


b) After oxidation of grid

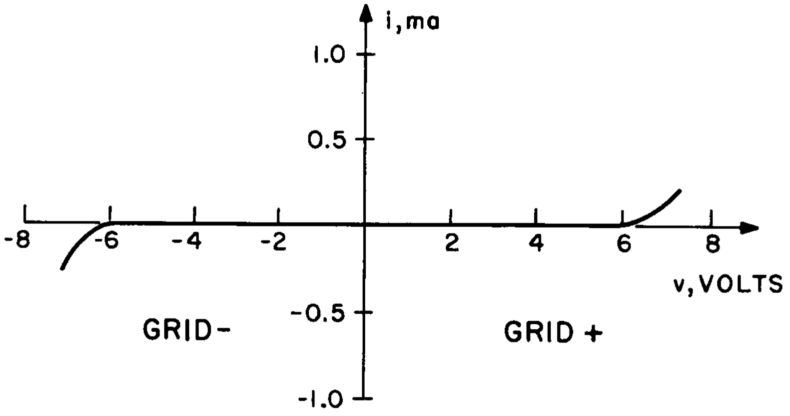


c) After deposition of second CdS layer

Fig. 10 The Grid-To-Electrode No. 1 as a Monitor of the Oxidation Process blocking contact to the CdS. Characteristics as shown in Fig. 11(a) were repeatedly obtained. The changes in electrical resistance of



a) Aluminum grid to electrode No. 1 diode



b) Aluminum grid to electrode No. 3 diode

Fig. 11 Aluminum Grid Insulation Characteristics

the electrode during formation followed the pattern described above, but took a much longer time to do so, and would, as annealing progressed, stop changing entirely. This might indicate that not only was the grid forming, but oxidizing as well, while the oxide inhibited further formation. Precautions were observed to initiate the formation cycle immediately upon completion of deposition of the aluminum, but work is definitely needed in investigating this problem. Profitable use may be made of atmospheres of inert gas in the evaporator, at low pressures during deposition, and at higher pressures during formation.

After formation, the grid structure was oxidized with the same apparatus as described for the silver grids. The discharge voltage was brought up from 500 volts dc at a rate of 100 volts every 10 minutes, then allowed to remain at 1500 volts for 30 minutes. At about 1000 volts the grid reached the maximum value of its resistance. Further increases in the discharge voltage did not change it. This was taken to be an indication that the surface of the electrode had indeed become passivated against further oxidation, since the non-conducting Al_2O_3 effectively removes material from the conductive bulk of the grid.

A typical electrode resistance immediately after deposition was 200 Ω. This resistance would increase to 300 Ω and stop during the 425° C formation cycle. As the insulating discharge proceeded, the grid resistance would increase, at first rapidly, then more slowly, and finally stop altogether at 700 Ω. The gold bolster material would then reduce this to about 300 Ω.

Depositing the second CdS layer caused no change in the v-i characteristic of the grid to electrode No. 1 diode. The v-i characteristic of the grid to electrode No. 3 diode was that shown in Fig. 11(b). Although this was excellent insulation, several of the devices were found to be "weak" in the sense that they could not withstand much over 10 volts without "burning out" and becoming a 100 Ω short. However, more than half (about 10 out of 15) were good devices, with the insulation characteristic indicated in Fig. 11(b). The operation of these devices as triodes is described in the next section. Using the techniques described here, it would seem that aluminum grids, once their formation properties have been ascertained, can be more than sufficiently insulated from the CdS in which they are sandwiched.

V. TRIODE OPERATION

A. "Normal" Mode of Operation

Fig. 12 shows the circuitry used for determining the properties of the devices when used as triodes.

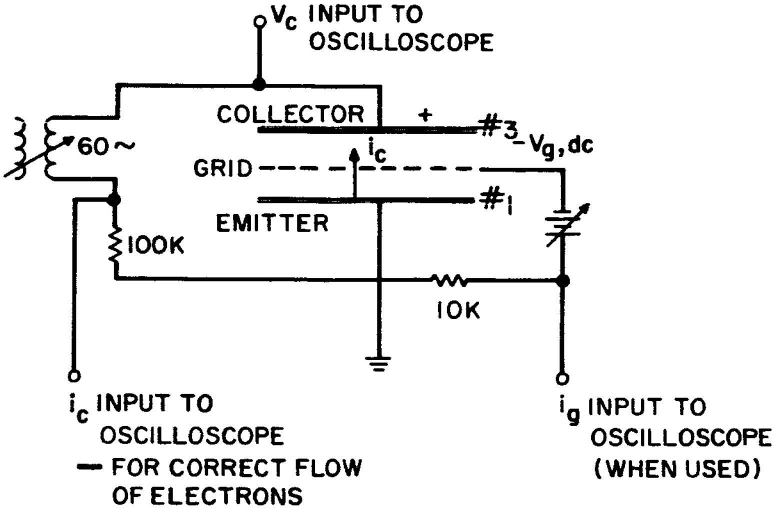
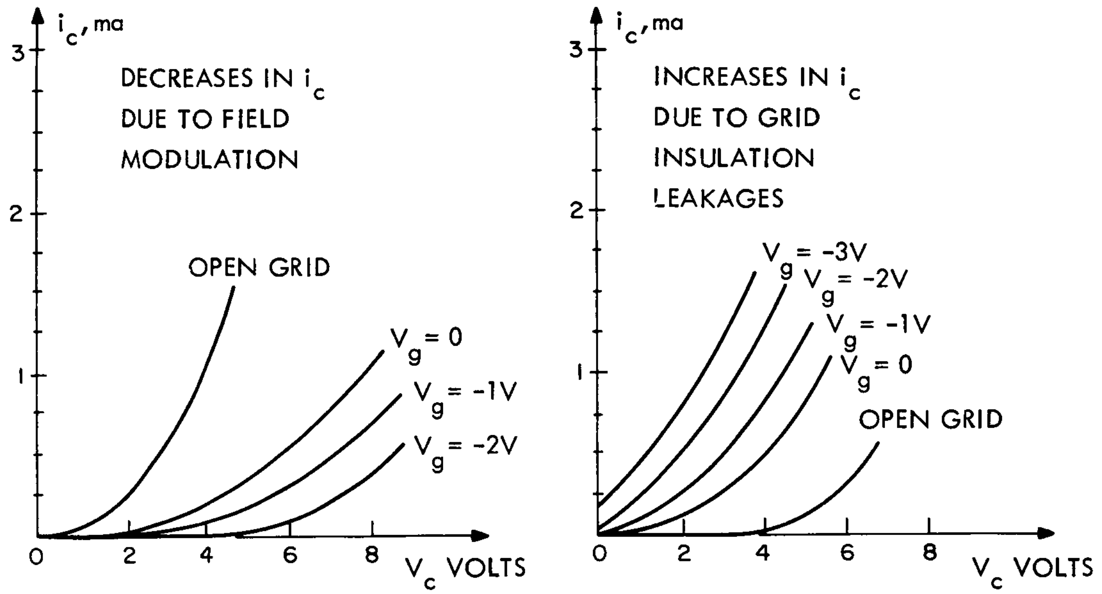


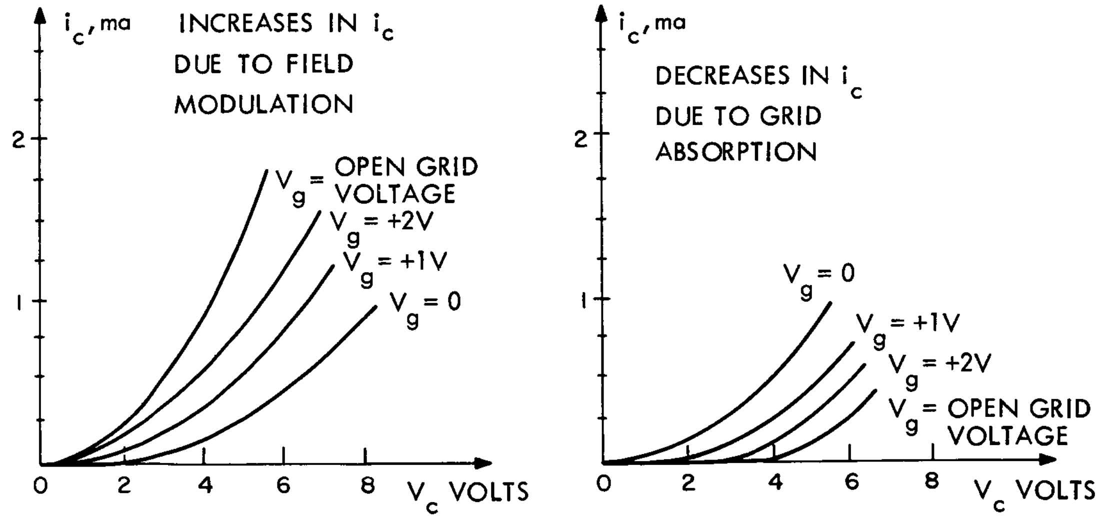
Fig. 12 Circuitry for Obtaining V-I Characteristics

Consider a perfect device. The grid-electrode No. 1 characteristic and grid-electrode No. 3 characteristic would be as shown in Fig. 11. Assuming that electrode No. 1 (ohmic contact) were connected as the emitter and electrode No. 3 (also ohmic) were to serve as the collector, the "plate" curves would appear as in Fig. 13(a). When the grid is disconnected, the v-i relation for collector to emitter would appear as the familiar "insulating layer" characteristic, because of the surface treatment applied between the two CdS layers. For negative grid voltage, the grid could not inject electrons. Then, if the conduction mechanism in the CdS were space-charge-limited, the "triode" curves would be generated. Note also that for an aluminum grid, the grid voltage can also be made positive up to about 4 volts without appreciable absorption of electrons from the CdS. Hence, it would be expected that the conduction "enhancement" curves would appear as in Fig. 13(b).



a) Ideal "plate" characteristics for normal device

c) Actual "plate" characteristics for normal device



b) Ideal "plate" characteristics for enhancement device

d) Actual "plate" characteristics for enhancement device

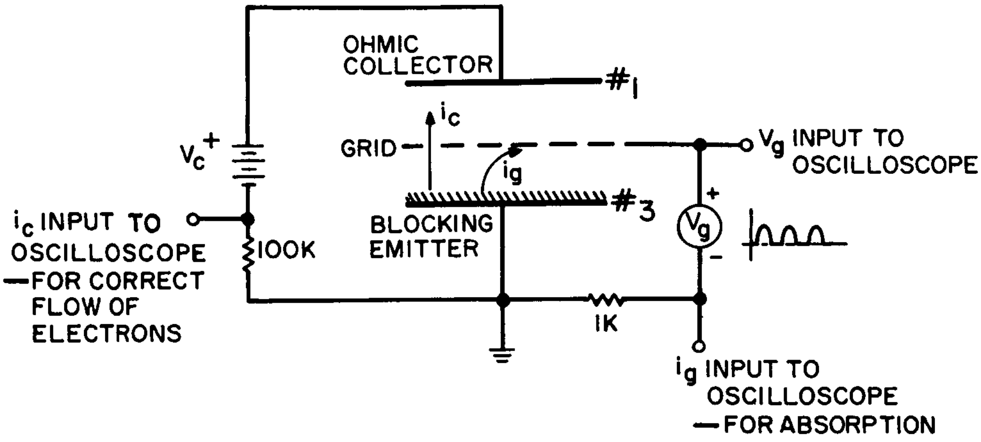
Fig. 13 Ideal and Experimental Plate Characteristics

Unfortunately, these have never been observed. No change in the plate curves is observed for small grid voltages, and for large grid voltages only the effect of insulation leakages is observed. For large negative grid voltages, the collector current increases by exactly the amount that the grid injects, while for large positive grid voltages it decreases by the amount that the grid absorbs. The actual curves are shown in Fig. 13(c) and (d). It is seen that there is entirely too much insulating material in the grid holes, most probably because they are too small. This clearly demonstrates the need for an investigation of the formation properties of aluminum grids.

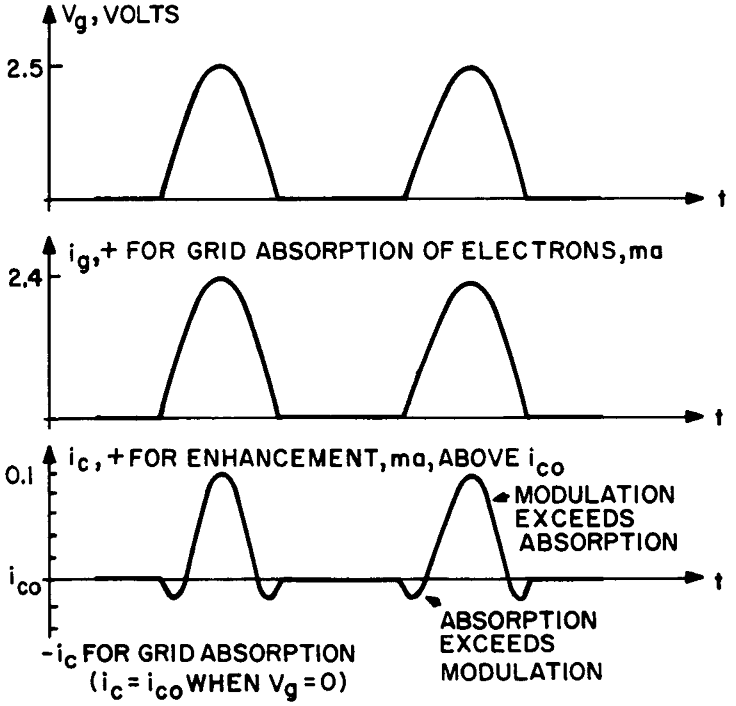
B. "Enhancement" Mode of Operation

There are several reasons for believing that the conduction process in the bulk of CdS thin-film deposits is not space-charge-limited. The most forceful reason is that the blocking character of an electrode is almost entirely dependent on the surface treatment of the CdS before its deposition. If a gold electrode is deposited on Type II CdS with no surface treatment, the device it forms with a bottom electrode is usually a 1K resistor. But in order that a grid be able to usefully modulate the flow of current, there must be a nonlinear conduction law between the grid and emitter. Since the only nonlinearity which can be introduced into a device is that produced by an oxygen discharge treatment, the only possible way of achieving the prescribed situation is to treat the CdS surface before deposition of electrode No. 3, and then to use electrode No. 3 as the emitter. It must be further noted that when such a device is properly biased (i.e., the collector No. 1, is positive), the blocking region is essentially back-biased. The emitter can inject almost no current. Then the only useful grid modulation which can be achieved occurs when the grid is positive. The positive grid voltage enhances the flow of current over the back-biased contact at the emitter.

Several devices were constructed to make use of this principle. Electrode No. 1, as always, made ohmic contact to the CdS. The aluminum grid was placed on top of CdS I (9600 Å thick) and insulated in the manner indicated above. The second CdS layer was then deposited (4800 Å thick) and its surface was treated to form a blocking contact with electrode No. 3 which was then to serve as the emitter. This



a) Circuit for determining operation of device

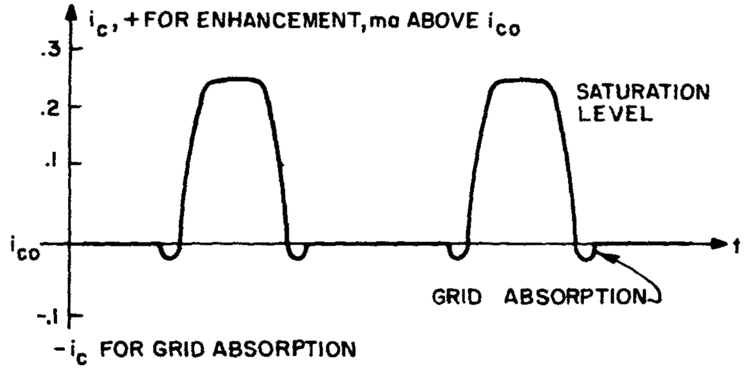


b) Time operation of device

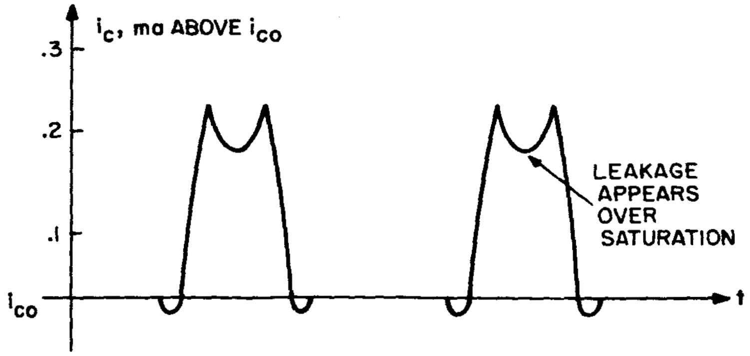
Fig. 14 Experimental Determination of Enhancement Operation procedure put the grid closer to emitter than collector, and it was hoped that this might enable the grid to effect more enhancement modulation for lower fields.

Figure 14 shows the operation of the device. The operation is presented in time-base because v-i plots become confusing for a device of this nature. Figure 14(a) shows the circuit used to obtain the curves. A constant dc potential was applied to the collector as shown. Figure 14(b) shows that as the grid voltage was increased positively, its absorption of current exceeded its modulation until modulation became so pronounced that it overcame the grid leakage. It is seen that under the conditions of bias in Fig. 14(a), collector current changes in the sense shown in Fig. 14(b) can only be due to modulation, since leakage registers in the sense opposite to modulation. It is further seen that the grid voltages required to effect modulation were very high--too high, in fact, for the device to produce gain. The device is not sensitive enough to small changes in grid voltage.

When the grid voltage exceeded the voltage on the collector, an interesting effect was noted as shown in Fig. 15. For grid



a) Saturation operation of device



b) Saturation with leakage

Fig. 15 Saturation Characteristics of Enhancement Device voltages slightly greater than the collector voltage saturation occurred as shown in Fig. 15(a). The reason for this saturation is that there is no field beyond the grid to move the charge to the collector, and the incremental current drops to zero just as in vacuum triodes. For even higher grid voltages, the grid current absorption again becomes prominent, and the curves assume the shape shown in Fig. 15(b).

It is seen, then, that operational devices can be fabricated with the techniques outlined in this report. They are, of course, useless with less than unit gain. If better grid parameters could be achieved with aluminum, and if the grid could be placed nearer, or possibly in, the blocking region of the emitter, it is not inconceivable that excellent active devices could be easily and cheaply fabricated.