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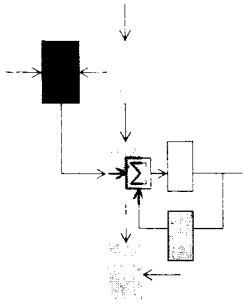

AN INVESTIGATION OF THIN-FILM GOLD STRUCTURES ON CdS

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by

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ABSTRACT

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Previous electron microscopic investigations of the structures of gold thin-films deposited on CdS surfaces have shown that these structures can be made electrically discontinuous with thermal treatments. This phenomenon is shown to exist for gold surface mass densities up to 30 $\mu g/cm^2$.

An investigation is made of the possibility that high electrostatic fields can be used to exert sufficient force on the discontinuous gold grains during annealing to cause the formation of "bridges" between them. It is shown that this procedure is not useful for the formation of grid-like structures.

A theoretical treatment is presented which shows that annealing phenomena can be explained with an atomic gold gas model. The theory predicts that "solid-layer" structures are not stable at high substrate temperatures.

A means of fabricating grid-like structures with 40-50% open area and sheet resistances of 12-50 Ω/sq. is described in detail. The method of production is found to be a consequence of the gas-model.

Author

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The efforts of the Drafting and Publications Staffs of the Electronic Systems Laboratory in preparation of this document are also greatly appreciated.

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I. INTRODUCTION

This report is concerned with the development of techniques for vacuum-depositing grid-like gold structures on CdS thin-film surfaces. The work is a continuation of an investigation reported in Electronic Systems Laboratory Report No. ESL-R-229, "An Electron Microscopic Investigation of CdS Thin-Film Surfaces". As was discussed in that report, there are four basic types of evaporated CdS surfaces which vary in the degree of their crystallinity and in the size of their surface asperity. These surfaces were found to have differing nucleation characteristics for small amounts of gold. It was also discovered that all of the surfaces had a high, uniform density of nucleation sites, so that any amount of gold over about 10 $\mu g/cm^2$ would form a completely continuous, "solid-layer" film. This property of the surfaces was considered undesirable because, in order to fabricate a grid-like structure, it must be possible to deposit a film which is at least partially discontinuous. It was discovered that heating the CdS-coated substrate during gold deposition produced a film which was completely discontinuous, and that annealing the sample after deposition seemed to produce a distribution of gold "agglomerates" of approximately uniform size and number density on the surface. This rule was strictly true for surface mass densities up to 8 $\mu g/cm^2$. These phenomena were explained in terms of a "liquid" film of gold, whose surface tension and adhesive force to the CdS surface was a function of temperature.

It is at this point that the work of this report begins. The experimental techniques and apparatus were essentially unchanged. The principal tool of the investigation was the electron microscope. The various specimen preparation techniques were also unchanged, but are explained again briefly in the interest of clarity.

There are four kinds of microscope specimens useful in this work, the preparation of all of which start with the deposition of a 3-400 Å carbon film onto the surface of the sample. This film, called a "replica", can be separated from the substrate in HCl -- the HCl dissolves the CdS and the replica floats free on the surface of the bath. This is called "stripping" the replica. If the gold of the sample

remains stuck in the replica after the CdS is dissolved, the replica is called "direct". If there is no imbedded gold, the replica is called "pure". A direct replica can be used for electron diffraction analysis of the gold structure imbedded in it. Metallic chromium can be evaporated from an angle onto the replica surface, a technique called "shadowing". If a direct replica is shadowed, details of the CdS surface become visible in the "background" of the micrographs, while the gold is observed directly. Such a specimen is called a "combination" replica. Note that an unshadowed pure replica is useless, because no detail would show up on the surface. Carbon thin-films are almost transparent to the electron beam, and gradations in the thickness of the film give insufficient contrast for photography. The fourth type of replica is made by stripping the carbon film from the substrate in very weak acid or in water. By varying the angle made by the substrate with the surface of the bath, the carbon can be made to separate from the gold or to pull the gold along with it. Alternate patches of direct and pure replica can thus be stripped side-by-side on a single carbon film. The specimen is shadowed, and the result is photographed microscopically right on the boundary line between the direct and pure areas. Such specimens are very useful aids in the interpretation of pure replicas.

The first step of this investigation was to examine the structure of gold films of high surface mass densities which were deposited at elevated substrate temperatures and low deposition rates, and were annealed for long periods. The purpose here was to see how high a surface mass density of gold can be deposited onto a CdS surface and still form an electrically discontinuous film. Surface mass densities as high as 30 $\mu g/cm^2$ were found to be discontinuous, but the thermal processing used had a disruptive effect on the CdS surface. The gold grains would penetrate the CdS surface to the extent that up to half of their mass was beneath it.

It is not yet known what effect this penetration has on the electrical properties of the structures on which it occurs, but it was assumed that penetration is accompanied by significant diffusion onto the CdS-gold interface region, and should be avoided where possible.

The shape of the grains produced by the high temperature processing was determined and measured with replica techniques. It

was discovered that a significant amount of material was missing -- it had either been removed by the acid-stripping process or had re-evaporated from the substrate. Calculations presented give strength to the conclusion that both losses occur. Considerations as to the physical nature of the processes involved in forming the structures seen in the micrographs gave rise to two possible models. The first of these was that of a "semi-fluid" agglomerate surrounding a core which is firmly fixed to the CdS surface. The semi-fluid is characterized by its surface tension and its fluid mobility on the surface about its core, both of which are affected by the temperature of the substrate. This model seemed to explain all of the processes which were observed in work previous to its formulation.

The second possible model was that of a gas of atomic gold which is in equilibrium with the solid structure on the surface. This gas would be characterized by its density and evolution rate -- both functions of substrate temperature.

An experiment was designed to simultaneously test the semi-fluid and core model and to investigate the possibility of forming "bridge" structures between the agglomerates of a gold film rendered discontinuous with thermal treatments. It was proposed that if the agglomerates were indeed fluid at high temperatures, then a voltage applied across the surface occupied by the structure at these temperatures should exert a measurable force between them, and possibly induce bridging. The results of the experiments show that bridging does occur, but only at surface mass densities which are quite high ($30\ \mu g/cm^2$). It was discovered that bridge formation depends on the presence of small agglomerates which are present only if the gold has been deposited at a fairly high rate onto a substrate held at a moderate temperature. The resulting structure was not "open" enough to be considered grid-like.

A simple calculation presented here shows that if the bridging process is to be explained by the semi-fluid model, the surface tension of the fluid must be of the order of 10^{-19} dyne/cm. The surface of such a fluid would not even have enough strength to confine its molecules against thermal bombardment. From this it was concluded that the physical process involved is essentially gaseous.

A mathematical model of the gaseous formation process was formulated and is presented in this report. Simple approaches to the representation of emission and absorption of gold atoms from hemispherical agglomerates are introduced, and the dynamics of an annealed system are considered. Equilibrium is defined for the gas-agglomerate system, and it is found that annealing will not alter the agglomerates on a surface provided that these agglomerates can reach an "equilibrium distribution". The evaporation process is then qualitatively considered, and the main conclusion of the treatment is that solid layer structures are not stable at high temperatures and low deposition rates. It is shown that for a given substrate temperature there corresponds a critical rate of deposition, which, if exceeded by the depositing source, requires that the resultant structure will be a solid layer.

It is argued that if a solid layer is not stable at low deposition rates, it is certainly not stable during annealing, where the deposition rate is zero. This argument is shown by experiment to be resoundingly true, and the outgrowth was a practical technique for grid fabrication. Solid layers were deposited and then annealed. The resultant structures are found to be grid-like with 40-50 percent open area and an aperture size of about 3000 Å. They also exhibit good electrical conductivity. A catalogue of evaporation parameters is presented for use in production of grids of various surface mass densities and aperture sizes. The process is discussed in terms of the gas model, and found not to invalidate it at any measurable point.

The electrical properties of the grids were explored and it is found that blocking contact can be made by a grid to a CdS surface only if the bare CdS is first treated with an oxygen discharge of 30 minutes duration. This process seems always to produce a blocking contact. A preliminary "triode" was fabricated, and it was found difficult to make a blocking contact to CdS which is deposited on top of the grid. Some modulation was definitely noted, however, for small grid voltages.

It is proposed that the subject of future work be an examination of the microscopic processes involved in making a blocking contact with a grid, and to study possible means of optimizing the active field-effect device.

II. HIGH SURFACE MASS DENSITIES

It has previously been discovered that low deposition rates and high deposition substrate temperatures coupled with long, high temperature post deposition thermal cycles can produce a completely discontinuous gold film on CdS surfaces. The main purpose of these experiments was to test this procedure for surface mass densities up to the normal working level for devices. The samples for the investigation were all made using the following procedure:

1. Depositing the CdS (Type II or IV).[1]
2. Heating the substrate to a thoroughly equilibrated temperature of 285°C. (Equilibrium was established in about 60 minutes.)
3. Slowly depositing the gold at a source temperature of 1300°C. (Rate of deposition ~3Å/min.)
4. Annealing the sample for 60 minutes at 285°C.
5. Cooling to room temperature in vacuum.

"Combination" electron microscopic specimens were then prepared in the usual way and the results are presented in Figs. 1-6. These figures show carbon replicas of gold on CdS surfaces from which the CdS has been removed with HCl, the gold remaining stuck on the replica. (These are called "combination" specimens.) Hence, the viewer observes the gold from inside the CdS layer--i.e., "underneath" the gold. If the replica is stripped from the sample at an acute angle between the slide and the surface of the HCl, the carbon can be separated from the gold as well as from the CdS. Such a "pure" replica shows the heights of the grains above the CdS surface. Both types of replica can be placed on the same microscope grid and shadowed.

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[1] The meaning of the four surface types of CdS deposits is described in M.I.T. Electronic Systems Laboratory Report ESL-R-229, "An Electron Microscopic Investigation of CdS Thin Films." The general techniques of these studies are described there as well.

Figures 1 and 2, combination specimens, show 10 $\mu g/cm^2$ of gold on Types II and IV CdS, respectively. Observe that the differences shown in earlier work between the nucleation characteristics of the two surfaces are not significant here.[2] This was seen to be true throughout these experiments. In these samples, the average grain size is 250 Å. Note the slight "undulations" observed in Fig. 1 which are due to the large surface asperity of the Type II surface. There are strange depressions in the CdS surface surrounding each grain, and it is obvious that each grain casts a shadow. This can only mean that the gold grains have penetrated the CdS surface. These facts are discussed in detail later. The penetration depth here is 50 - 60 Å.

Figure 3 shows 15 $\mu g/cm^2$ of gold deposited on CdS under the same conditions. The grain size of this structure is 375 Å and the penetration depth is 210 Å. The height of the structures above the average CdS surface can be measured on a "pure" replica (one from which the gold has been removed.) This height for the 15 $\mu g/cm^2$ structure is ~175 Å. Note that this means that a significant amount of the gold has penetrated the surface.

Figure 4 shows 20 $\mu g/cm^2$ on Type II CdS. Even the slight undulations visible in Fig. 1 are no longer seen, indicative of the fact that grain sizes are of the order of magnitude of the CdS asperity, and that the CdS surface is appreciably changed by gold penetration. The grain size for these structures is 500 Å, their average depth of penetration is 150 Å, and their height above the surface is 75 Å as measured from a pure replica. Figure 5 shows a pure replica for the same sample right on the boundary line of an area where the gold has been left attached. Such photographs are of great aid in the interpretation of pure replicas, which can become quite complicated with respect to the appropriate senses of "rise" and "depression". The arrow shows a place where a grain rose particularly high above the surface. Evidence such as this gives the principal information about the peculiar structure assumed by the gold grains in these experiments.

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[2] M.I.T. Electronic Systems Laboratory Report ESL-R-229.

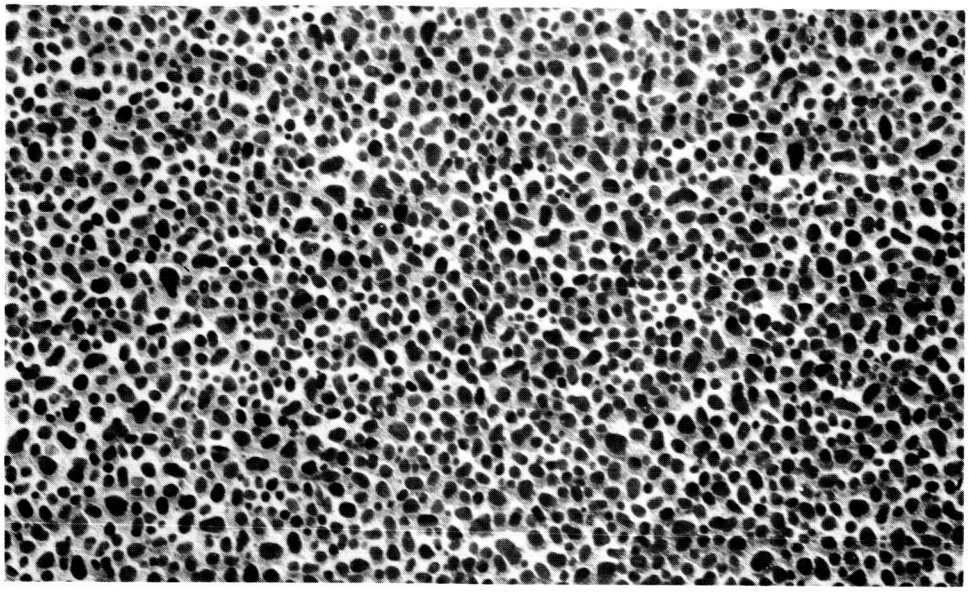

Fig. 1 10 $\mu g/cm^2$ gold on Type II CdS surface. Grain size 250 Å, penetration depth about 60 Å. Combination replica, 80,000 x.

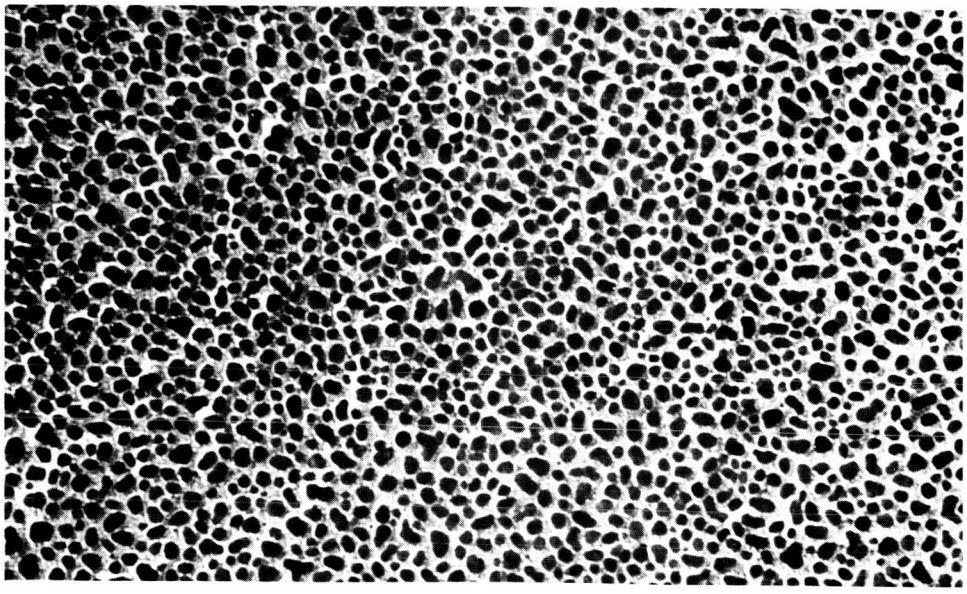

Fig. 2 10 $\mu g/cm^2$ gold on Type IV CdS surface. Grain size 250 Å, penetration depth about 60 Å. Combination replica, 80,000 x.

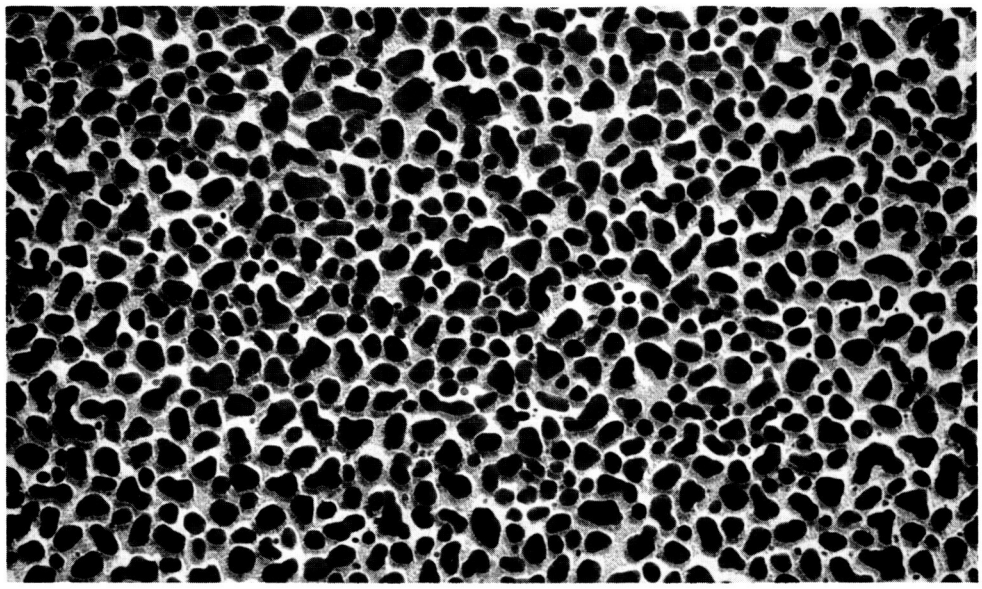

Fig. 3 15 $\mu g/cm^2$ gold on Type II CdS surface. Grain size 376 Å, penetration depth 210 Å. Combination replica, 80,000x.

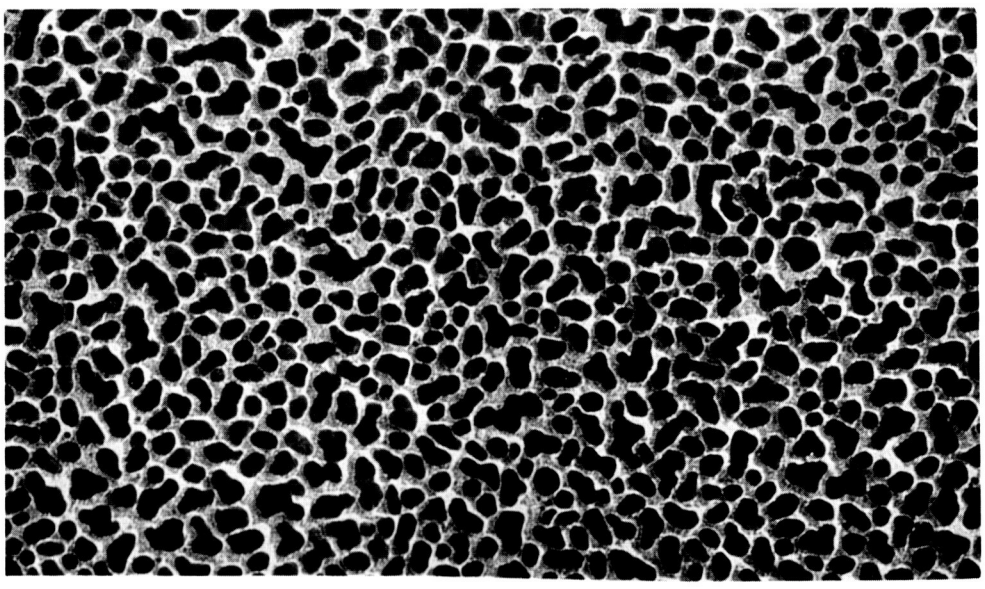

Fig. 4 20 $\mu g/cm^2$ gold on Type II CdS surface. Grain size 500 Å, penetration depth 150 Å. Combination specimen, 80,000x.

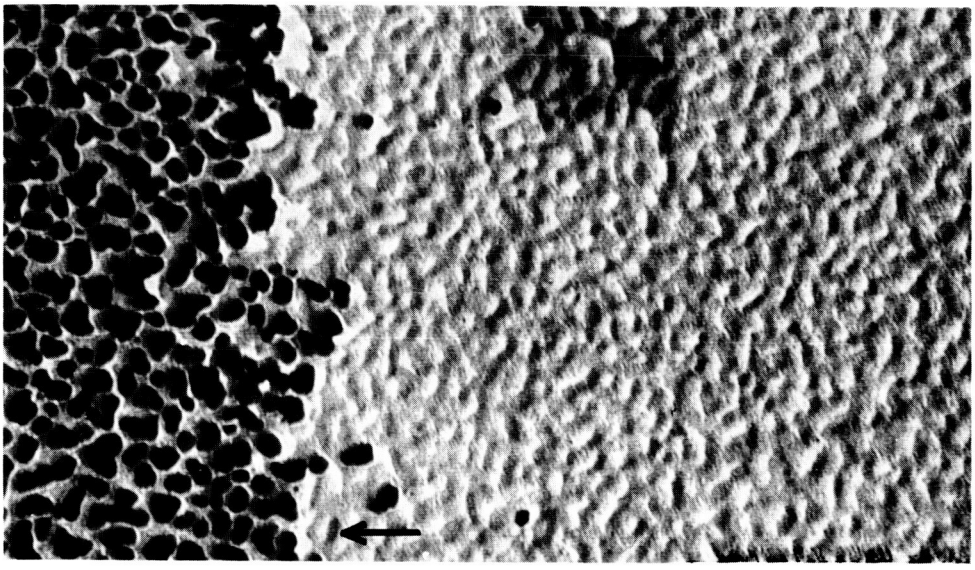

Fig. 5 Pure and combination replica shown on boundary line for sample of Fig. 4. Average grain height 75 Å. Arrow shows replica of particularly high grain. (80,000 x).

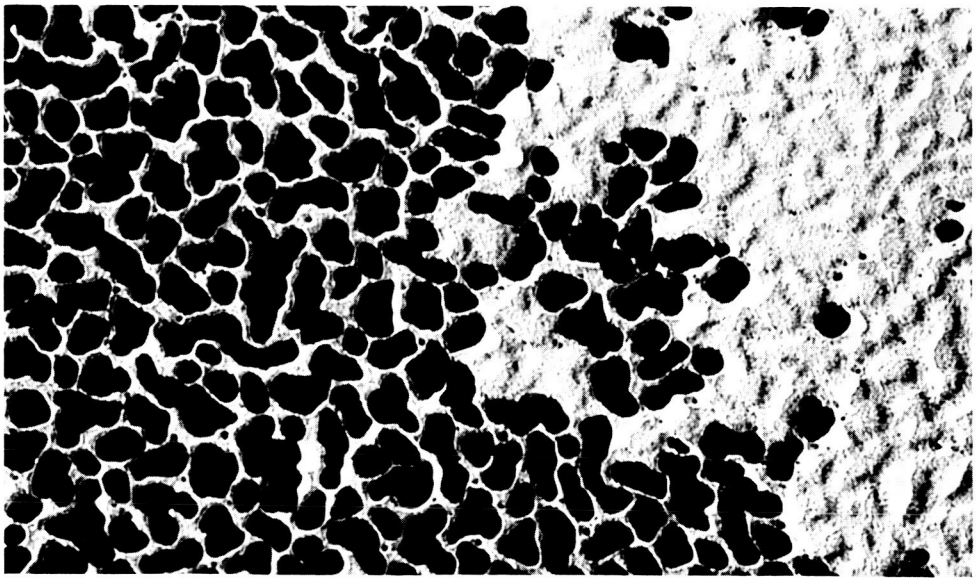

Fig. 6 30 $\mu g/cm^2$ gold on Type II CdS surface. Grain size 625 Å, height above surface 145 Å, penetration depth 290 Å. Pure and combination replica, 80,000 x.

Figure 6 shows a boundary of pure and combination replica for 30 $\mu g/cm^2$ deposition of gold on a Type II surface. The grain size of the structures is 625 Å, their height above the surface is 145 Å, and their penetration depth is 290 Å. No particularly sharp rises above the CdS (as in Fig. 5) are seen.

A careful but approximate quantitative analysis was made of this data, with the result that surface mass densities measured directly from the micrographs account for less than two-thirds of the surface mass density calculated from Knudsen's cosine law with a carefully weighed charge of gold in the evaporator. In addition, the depression surrounding each gold grain remained unexplained. The only model for the grain structure which explained these facts is shown in Fig. 7.

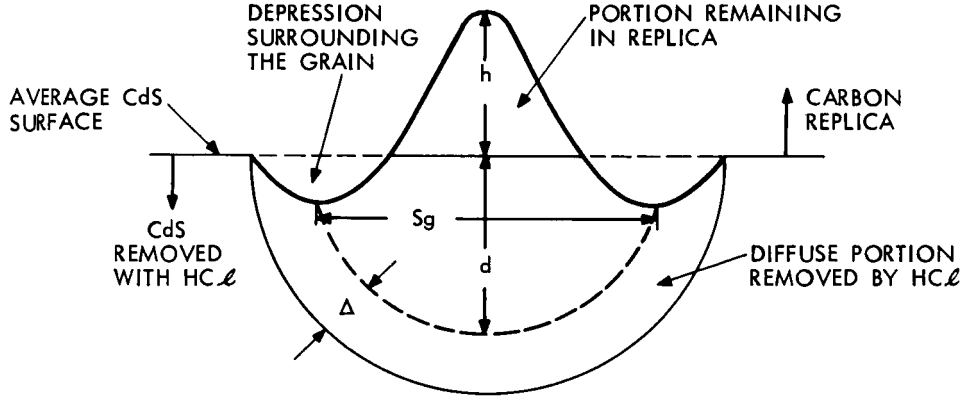

Fig. 7 Structure of a heavily heat-treated gold grain in schematic cross section

The portion of the grain below the CdS surface can only get there by a solid diffusion process and is assumed not to be solid gold. This could explain the ease with which HCl removed the outer portion, Δ, of the grain. The shape of the grain is prescribed by evidence such as that shown in Figs. 5 and 6. The 30 $\mu g/cm^2$ structure does not have such a pronounced depression, while the deepest depressions were observed on the 15 $\mu g/cm^2$ specimens.

The volume of each grain was calculated using the assumption that the portion of the grain which remains imbedded in the replica was not corroded by the HCl. The volume of the grain present on the replica (i.e., the portion

imbedded in the replica plus the unremoved sub-surface portion) was approximated by the ellipsoid:

$$V_p = \frac{4\pi}{3} \frac{S_g^2}{4} \left(\frac{h+d}{2}\right)$$

$$= \frac{\pi}{6} S_g^2 (h+d)$$

where

h = height of grain above surface

d = depth of penetration into surface

S_g = average grain size, as shown in Fig. 7

V_p = volume present on replica of each grain

The volume of each grain removed by HCl was approximated by the hemispherical shell:

$$V_\Delta = \left(\frac{1}{2}\right) \frac{4\pi}{3} \left[(d+\Delta)^3 - d^3\right]$$

where Δ = the thickness of removed portion, as measured from the photographs. This thickness was assumed to be equal to the width of the depression surrounding each grain as shown in Fig. 7. The results of these calculations are shown in Table 1. Each entry represents a sample from which the data was obtained from several micrographs. It is seen from the table that larger percentage corrections for acid removal are necessary for smaller grains. It was found that deeper surface penetration for a given grain size occurred on Type IV than on Type II. The correlation of this model with the actually deposited surface mass density is shown in Table 2.

Table 1

	μ_{meas}	S_g	d	h	Δ	V_p	V_Δ	V_g
	14.5	376	216	98	50	8.85	8.70	17.55
	14.4	250	144	72	40	7.07	6.80	13.87
	19.6	500	144	72	30	28.2	4.92	33.12
	19.6	500	144	110	30	29.4	4.92	34.32
	30	625	288	144	50	88.0	30.4	118.4
Units	$\mu g/cm^2$	(Å)	(Å)	(Å)	(Å)	$(x\ 10^6)$ $(Å^3)$	$(x\ 10^6)$ $(Å^3)$	$(x\ 10^6)$ $(Å^3)$

Where μ_{meas} = surface mass density calculated from weight of gold charge and

$V_g = V_p + V_\Delta$, the total average volume of a grain

Table 2.

	μ_{meas}	V_g	$\overline{N}$	μ_{calc}
	14.5	17.55	26	14.0
	14.4	13.87	28	13.0
	19.6	33.12	19	19.4
	30	118.4	8.75	31.6
Units	$\mu g/cm^2$	$\times 10^6$ Å^3	No. grains per unit area	$\mu g/cm^2$

Where μ_{calc} is the surface mass density calculated from the microscopic data. Here, $\overline{N}$ represents the equivalent number of average grains per unit area of the sample, and the bulk value of mass density has been assumed. The unit area taken for $\overline{N}$ was 6.25×10^6 Å^2, (which is a square 2 cm. on a side in the figures of this report). This was large enough to represent the entire specimen on a statistical basis.

It is seen from Table 2 that the results of the calculation agree very well with actual values, a fact that gives considerable confidence to the model used for the grain structure. The precise shape of the grain shown should not be taken too seriously, but it must be true that they have a considerable portion of their mass below the CdS surface. The model indicates that this portion may be better than half of their total mass, but it is conceivable that a smaller amount of material was actually dissolved away while some above-surface material was re-evaporated from the sample. Some of the observations in later sections give strength to this possibility. In any case, a significant penetration of the CdS definitely occurs during high temperature-long time thermal cycles.

The mechanism of such a penetration could be initially one of diffusion, followed by a sub-surface agglomeration of gold atoms. This would only occur immediately under a grain so that after long times the effect would be one of penetration. The sub-surface material might well be spongy--the holes of the sponge filled with CdS. It would not then be surprising that such a structure would easily be attacked by HCl, even though past work has shown that the acid stripping process does not

remove significant amounts of gold. The result of these experiments which is of principal importance to device work is that surface mass densities of gold as high as 30 $\mu g/cm^2$ can be made completely discontinuous on CdS surfaces while, without such thermal treatments, surface mass densities as low as 15 $\mu g/cm^2$ form completely continuous solid layers. The physical mechanism by which this technique operates was thought, at this point, to be due to one of two processes.

The first of these processes models the gold grains on the hot, coated substrate as a "semi-fluid"[3] surrounding a solid core which is firmly fixed to the CdS surface. The principal features of a semi-fluid are its surface tension and its "fluid mobility"--i.e., the atoms of the material can move on the surface about the core as a fluid governed only by the adhesive forces of the surface underneath. This qualitative model was introduced to explain the phenomenon of coalescence seen often in previous work. Two small agglomerates of atoms on a CdS surface seem to coalesce when the surface is heated in much the same way as two raindrops on a windowpane do when they touch. The result is an elongated single agglomerate of larger size. The elongation in the case of the raindrop is due to adhesive forces from the glass, while for the gold agglomerate, it is due to implantation of the core. Some coalescences are forceful enough to uproot the core of one of the agglomerates. The surface mobility and fluidity of the semi-fluid occur only at high temperatures. This model explains why the solid layer occurs without thermal treatments. CdS was found to have a high uniform density of active nucleation sites for gold, and, as deposition proceeds, the enlarging agglomerates, lacking the confining surface tension of the semi-fluid and its mobility are forced into a polycrystalline, continuous solid layer. If such a model is correct, it was reasoned, then it should be

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[3] The idea of a semi-fluid and core model is not new. It seems to describe crystallization in thin carbon films at elevated temperatures very well. See N. Fuschillo et al., Journal Applied Physics, 36, 575 (1965).

possible to force coalescence or at least "bridging" between agglomerates with electrostatic forces from a high voltage applied across the film, provided that the surface tension of the semi-fluid was not too great and its mobility not too small. Experiments designed to test this reasoning are described in the next section.

The model for the other of the two possible processes--that of an atomic gas in phase equilibrium with solid agglomerates fixed on the CdS surface is described in detail in Section IV of this report.

III. EXPERIMENTS WITH VOLTAGE FORMATION

Once having developed a technique for producing completely discontinuous gold films of any reasonable surface mass density, it was thought that the next step in the production of grid-like structures was to form interconnecting bridges between the agglomerates. It was hoped that the resultant structure would then be "lacy", but electrically continuous. The technique by which it was hoped to form such bridges was voltage formation.

If the semi-fluid and core model is considered, it is evident that a large voltage applied across a heated gold film will produce some force of attraction, however small, on the metallic semi-fluids of two adjacent agglomerates. This force would pull against the surface tension forces of the semi-fluids. Hopefully, the adhesive forces from the CdS become negligible at high temperature except for those on the firmly implanted core. As the electrostatic force increases, an instability will develop on the surface of one of the semi-fluids and an immediate bridging will occur.

An experiment was designed to test this theory. A set of samples of varying surface mass density from 5 to 30 $\mu g/cm^2$ were deposited on Type II CdS. Electrical contact to the gold film during fabrication was furnished by two 300 Å gold electrodes which overlapped the CdS. These were connected with silver paint to spring contacts and wires leading outside the evaporator. Voltage and current through the sample were monitored throughout the gold deposition and annealing. The gold was deposited and annealed for 30 minutes at a substrate temperature of 140°C, and at an applied voltage of 100 volts across 1.75 cm. of sample. Two areas were deposited for each sample, one of which was connected with high voltage, and the other of which was free of all electrical contact.

The electron microscopic comparison of the two patches showed absolutely no difference caused by the application of the high voltage except in the case of the 30 $\mu g/cm^2$ sample. Figure 8 shows a combination specimen for the untreated area of the sample. This film was deposited and annealed at a lower temperature and for a shorter time than its counterpart of Section II, (Fig. 6). This has caused the grains

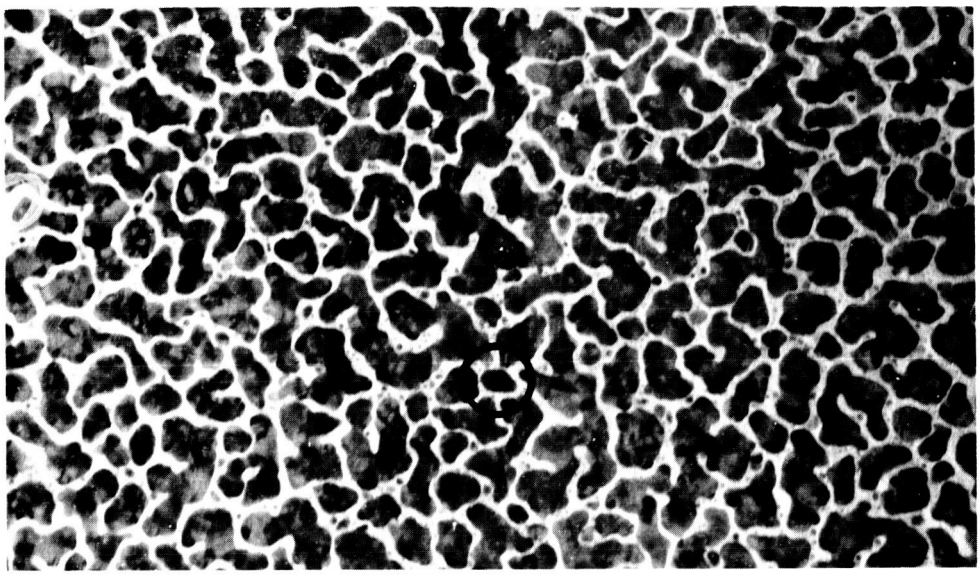

Fig. 8 30 $\mu g/cm^2$ gold on Type II CdS, annealed with no applied field. Circle indicates optimum conditions for bridging. Direct specimen, 80,000 x.

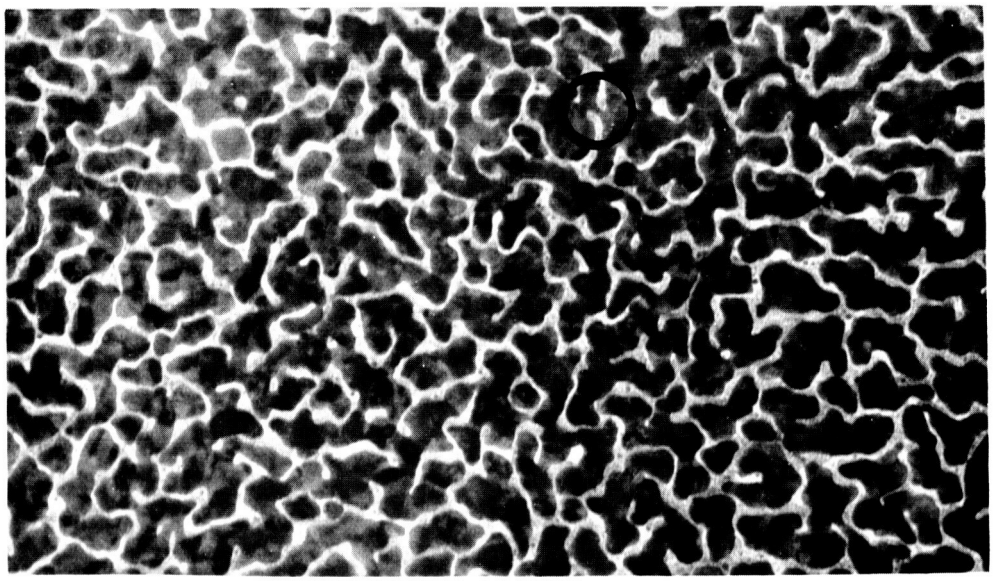

Fig. 9 30 $\mu g/cm^2$ gold on Type II CdS surface, annealed with applied field of 100 v. across 1.75 cm. Circle indicates a formed bridge. Direct specimen, 80,000 x.

to be somewhat larger in size, and the appearance of grains of two distinctly different sizes.[4] The large grains average about 1000 Å in size, while the small ones average 150 Å.

Figure 9 shows the voltage-formed section of the specimen. Note the complete disappearance of the small grains and several instances of bridging between large agglomerates. The sheet resistance of the unformed area was $\approx 10^3$ Ω/sq., while that of the formed area was 10^6 Ω/sq, a factor of 10^3 greater.

These results were interpreted using the semi-fluid and core model and a simplified geometry of the situation. Figure 10 shows the model

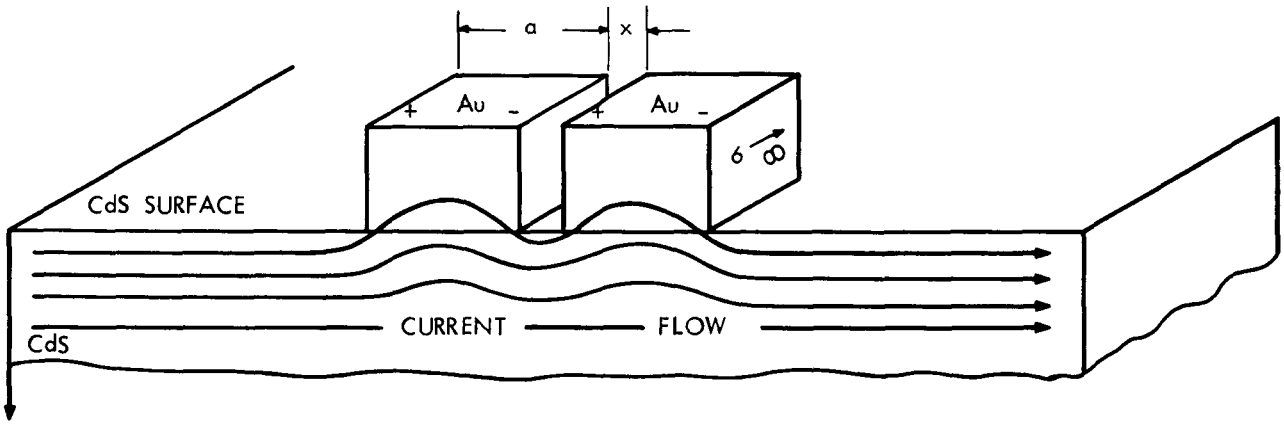

Fig. 10 Geometry for obtaining force of electric origin

of the structure used to obtain an expression for the electrostatic force. A uniform potential gradient along the length of the CdS substrate is assumed. The blocks make ohmic contact to the CdS and the potential difference between the two adjacent faces is determined by the distance between their outer faces, since the blocks are of infinite conductivity.

Hence, V, the potential difference between the faces, is

$$v(x) = E_o(2a + x)$$

where E_o is the assumedly uniform electric field applied between the 300 Å voltage electrodes. Then, q, the charge on the inner faces is,

[4] See Section IV of this report.

$$q(x) = \frac{\epsilon_o A E_o}{x} (2a + x)$$

The energy storage relation for such a "capacitor" is

$$dW = vdq + f_e dx$$

Then, since the system is conservative, W is a state-function and

$$f_e = \frac{vdq}{dx} - \frac{dW}{dx}$$

$$= \epsilon_o A E_o^2 \left[\frac{2a + x}{x} - \frac{(2a + x)^2}{x^2} \right]$$

$$- \epsilon_o A E_o^2 \left[\frac{2a + x}{x} - \frac{(2a + x)^2}{2x^2} \right]$$

or $$= - \frac{\epsilon_o A E_o^2}{2} \left[\frac{2a + x}{x} \right]^2 \quad \text{Attractive}$$

Then the force per unit area on the adjacent faces of the blocks is

$$P_e = - \frac{\epsilon_o E_o^2}{2} \left[\frac{2a + x}{x} \right]^2$$

The result can then be applied to the situation of voltage formation of semi-fluid structures. Replacing a with S_g, the size of a grain, P_e can be taken as an approximation to the pressure difference across the surface of the semi-fluid caused by the field. The surface tension of the semi-fluid can be modeled with the well-known phenomenological relation

$$\Delta p = \gamma(1/R_{||} + 1/R_{\perp})$$

where Δp is the pressure difference across the surface of the semi-fluid and R is the radius of curvature of the surface of the grain considered. Here the curvature of the fluid surface in a plane perpendicular to the substrate is neglected as being very small -- only the curvature in the plane parallel to the substrate is considered. Then, for the applied field to have an effect, the electrostatic pressure must be of the same order of magnitude as the surface tension pressure. Hence, as a condition for bridging,

$$\frac{\gamma}{R_{||}} = \frac{\epsilon_o E_o^2}{2} \left[\frac{2S_g + x}{x}\right]^2$$

In Fig. 8, S_g = 1000 Å; s = 125 Å, so x can be neglected in the numerator on the right, and

$$\frac{\gamma}{R} = 2\epsilon_o E_o^2 \left(\frac{S_g}{x}\right)^2$$

In this experiment, E = 100 v/1.75 cm, or $E_o^2 = 3 \times 10^3 v^2/cm^2$.

It was found, by constructing a model of the field situation on Teledeltos paper, that an irregularly shaped grain with a very small radius can "amplify" the field between two adjacent grains by a factor of 50 above the magnitude calculated from the simple block model. Taking this factor into account, but retaining the formula for pressure difference given by the block model $E_o^2 = 7.5 \times 10^6 v^2/cm^2$ or $2\epsilon_o E_o^2 = 13$ dynes/cm^2. The measured ratio S_g/x is ~8. Hence

$$\frac{\gamma}{R} = 832 \text{ dynes/cm}^2$$

A situation which fulfills the above criterion of having an extremely small radius of curvature is circled on Fig. 8; a bridge that might have been formed by this mechanism is circled on Fig. 9. The radius of curvature in Fig. 8 is about 50 Å or 5×10^{-7} cm. This gives a value for γ of 4.2×10^{-4} dyne/cm, about 4 orders of magnitude smaller than any substance commonly described by surface tension.[5] This fact forces the conclusion that a semi-fluid, if it existed anywhere in nature, would not have sufficient surface tension to confine its molecules against their thermal energy. Hence, the model assumed is invalid and was abandoned in favor of a gas of gold atoms in thermal equilibrium with completely solid agglomerates. Since the amount of gold gas emitted by the agglomerates is directly proportional to their surface area, the equilibrium structure assumed by the grains might be one in which the surface-volume ratio is minimum.

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[5] For molten gold at 1070°C, γ = 580 dyne/cm; for water at 10°C, γ = 74 dynes/cm.

This is precisely the minimal principle which governs a fluid and explains why the grains seem to behave as if they were fluid. Bridging may be accomplished by atoms moving in the inhomogeneous electric field. Possibly they become trapped at a point where the field is uniform (since the net force on a polarized particle in a uniform field is zero). The net buildup of material at such points could cause bridging. It should be noted that a particle trapped in the field would probably have enough thermal energy to escape and bridging would occur only rarely. Bridging would be especially likely at a place where adjacent grains are very close together -- as is the case for a large and small grain in Fig. 8. The fact that bridging occurs is probably directly related to the presence of these very small grains. They were not present on any but the 30 $\mu g/cm^2$ sample, the only one for which bridging was noted. The small grains can coexist with the large ones only at temperatures too low for the gas-solid equilibrium to be established. The concept of an equilibrium grain size for a given surface mass density is described in the next section.

Another fact of importance emerged from these experiments. The current line drawn in Fig. 10 shows that the presence of a highly conducting medium on the surface of a poor conductor perturbs the path of current upwards. This implies that if gold is making ohmic contact with the CdS at some point, larger current will be drawn through the gold-CdS interface than if that contact were blocking. If the contact were blocking, the path through the gold would be open-circuited at either the entrance or the exit. The higher current through the ohmic contact would cause local heating and increased emission of gold atoms from the heated grain. The result would eventually be the destruction of all or part of that grain. This may be the explanation of the 10^3 greater sheet resistance of the voltage-formed structure. There is less "shorting" of the CdS surface because the shorting material has been forced to move away. The outcome of a more careful investigation of this phenomenon may prove very fruitful to device work.

IV. THE CONCEPT OF THE EQUILIBRIUM SIZE

It was noted throughout the previous work that when a gold film is made discontinuous with thermal treatments, the grain size always assumes a uniform value over the entire surface of the sample with very small deviations.

It was hoped that this phenomenon could be described using a crude mathematical representation of the gas-solid model. The intention of this treatment was to obtain a maximum of understanding with a minimum of mathematical complication. For this reason, the classical thermodynamic approach to a treatment of the phase equilibrium situation is not used. The resulting simplification will become evident later.

The mechanism can be broken into 3 distinct processes.

1. Emission of gold atoms from the agglomerates.
2. Absorption of gold atoms from the surface gas.
3. Nucleation of new grains onto the CdS surface. In the interests of simplicity only situations of nearly total coverage of CdS surface were considered, and this process is neglected.

Processes 1 and 2 are modeled as simply as possible in order to obtain analytic expressions for their dependence on geometry and temperature.

A. EMISSION

Consider the surface of a single agglomerate. At high temperatures, the atoms on this surface can be modeled as oscillators in the plane of the surface, bound to the solid in the direction normal to the surface by the bond energy. The Boltzmann distribution is relevant to emission at high temperatures. Take this to be

$$W(\vec{p})\, d\vec{p} = \frac{d\vec{p}\,\epsilon^{-p^2/2mkT}}{\int_{-\infty}^{\infty} d\vec{p}\,\epsilon^{-p^2/2mkT}}$$

where $\vec{p}$ is directed outwards, but not necessarily radially. Strictly speaking this is erroneous, but the geometric factors which should be introduced are of small importance compared with the error which

would be incurred in approximating the resultant integral. The integral introduced above can be evaluated with a fair degree of accuracy.

The fraction of surface atoms having outward-directed momenta sufficient to overcome the bond energy is

$$f = \frac{2\pi \int_{P_b}^{\infty} p^2 \epsilon^{-p^2/2mkT} dp}{4\pi \int_{0}^{\infty} p^2 \epsilon^{-p^2/2mkT} dp}$$

where

$$P_b = \sqrt{2mE_b}$$

E_b = bond energy

The denominator is a standard form, which results in

$$(2\pi mkT)^{3/2} f = 2\pi \int_{P_b}^{\infty} p^2 \epsilon^{-p^2/2mkT} dp$$

$$= 2\pi(2mkT)^{3/2} \int_{x_b}^{\infty} x^2 \epsilon^{-x^2} dx$$

where

$$x = \frac{p}{\sqrt{2mkT}}$$

and

$$x_b = \sqrt{\frac{E_b}{kT}}$$

The bond strength for an atom on the surface of the crystal is half of that for an atom in the solid. Hence,

$$E_b = \frac{1}{2}(56.8 \times 10^{-13}) \text{ ergs/bond}$$

$$= 28.4 \times 10^{-13} \text{erg/bond;}$$

then

$$x_b^2 = \frac{E_b}{kT} = 37$$

at a temperature of 550°K. (277°C.). The integral on the right hand side can now be approximated by parts.

$$\frac{\sqrt{\pi}}{2} f = \int_{x_b}^{\infty} x^2 \epsilon^{-x^2} dx$$

$$= \left[-\frac{1}{2} x \epsilon^{-x^2} \right]_{x_b}^{\infty} + \int_{x_b}^{\infty} \frac{\epsilon^{-x^2}}{2} dx$$

Then

$$\int_{x_b}^{\infty} (x^2 - \frac{1}{2}) \epsilon^{-x^2} dx = \frac{x_b}{2} \epsilon^{-x_b^2}$$

The first term in the integral on the right is of order $x_b^{3/2}$, the second of order $x_b^{1/2}$. But $x \sim 6$, so the neglect of 2.4 with respect to 15 introduces an error of at most 20 percent. Thus,

$$\frac{\sqrt{\pi}}{2} f = \int_{x_b}^{\infty} x^2 \epsilon^{-x^2} dx \approx \frac{x_b}{2} \epsilon^{-x_b^2}$$

or

$$f \cong \frac{\epsilon^{-x_b^2} x_b}{\sqrt{\pi}}$$

At a temperature of 277°C, f is of order 10^{-16}.

The emission rate of gold atoms from an agglomerate can now be calculated. It is given by

$$E = \nu f \bar{v} (2\pi S^2)$$

where

ν = The number of gold atoms per unit volume at the surface.

$\bar{v}$ = The average velocity of emitted atoms.

$2\pi S^2$ = Surface area of a hemispherical agglomerate.

Note that the use of the post emission velocity to obtain the rate is only an approximation, but is one frequently used in statistical mechanics for estimating magnitudes.

Assumedly, an emitted atom immediately comes into equilibrium with the surrounding gas, and its average velocity is equal to that of the gas. Hence,

$$\bar{v} = \sqrt{\frac{3kT}{m}}$$

and

$$E \cong 2\sqrt{\pi}\, \nu \sqrt{\frac{3kT}{m}} \sqrt{\frac{E_b}{kT}}\ \epsilon^{-E_b/kT} S^2$$

$$\cong 2\sqrt{\pi}\, \nu \sqrt{\frac{3E_b}{m}}\ \epsilon^{-E_b/kT} S^2$$

but $\nu \cong 3 \times 10^{22}/cm^3$ for crystalline gold, and $m = 3.27 \times 10^{-22}$ grams/atom. Hence, $E \cong 1.71 \times 10^{12}\, \epsilon^{-E_b/kT} S^2$ for S in Å. At a temperature of 277°C with a grain radius of 100 Å,

$$E = 1.6 \text{ atoms/sec}$$

A grain of radius 100 Å contains about 6×10^4 atoms -- if not for absorption, such a grain would vanish in 10 hours; a grain of radius 50 Å, due to its smaller emitting surface, vanishes in about the same time.

B. ABSORPTION

Consider the gas produced by emission. It is, at the temperatures relevant here, a Boltzmann gas of free atoms constantly colliding with the agglomerates which produce it. Many of the collisions will result in the bonding of an atom to the crystalline agglomerate. The approximation made here is that all such collision result in bonding. Absorption rate is then directly related to the number of collisions suffered by the gas with an agglomerate per unit time. Figure 11 shows the geometry to be used in this calculation. Let the density of the gas surrounding the grain be uniform. Almost all the collisions will be from atoms having momenta in the plane parallel to the substrate, since any with a vertical component will leave the substrate, and there is nothing to force their return. Then only the atoms contained in the infinitesimal volume

$$\Delta v = 2\pi S^2 \bar{v}_p \Delta t$$

are destined to collide in Δt. Hence, the number of collisions per unit

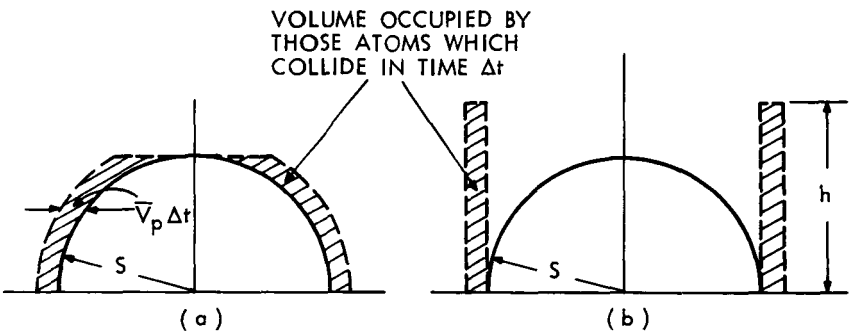

Fig. 11 Geometry for calculating rate of absorption

time is $2\pi S^2 \bar{v}_p n$ where $\bar{v}_p$ is the average velocity parallel to the substrate and n is the density of the gas.

Now deform this element to the shape shown in diagram (b), retaining its volume. It becomes a cylinder, rising to an arbitrary height h above the surface. Since n is uniform, the number of atoms contained in the deformed volume is the same as that in (a), but the number of collisions per unit time is now given by

$$2\pi Sh \bar{v}_p n$$

But

$$nh = N_g$$

where N_g is the number of gas atoms per unit area of the surface. This will be called the surface density of the gas.

It is here that the intrinsic difficulty of dealing with such systems emerges. The question of the size of the volume in which the gas is contained must eventually be answered in some way. It is obvious that, for a specimen in vacuum, there is no confining force, and the answer to the question is proved by defining an "effective gas thickness" h.[6] Surface physics often treats a two-phase system such as this in strictly two dimensions, but such a model would be unphysical here since

[6] This is not to be taken to mean that the gas is confined within this thickness, but that h is the thickness of the gas which interacts with the agglomerates. The effective volume of the gas is that of the evaporator, but most of the atoms in this situation never leave the substrate. See Section V.

this treatment considers the structure of agglomerates in three dimensions. It is also evident why thermodynamics would be very difficult to apply to this system. The goal of any thermodynamic treatment is the equation of state, and this equation cannot exist in the absence of a definition of volume. For this reason, a thermodynamic treatment has been avoided, with a consequent loss of information. This point is discussed in more detail later.

The number of atoms absorbed, then, per unit time, for a grain of radius S is

$$A = 2\pi S \bar{v}_p N_g$$

where $\bar{v}_p$ is given by

$$\bar{v}_p = \frac{1/m \int_{-\infty}^{\infty} dp_\phi \int_0^{\infty} dp_r \, p_r \epsilon^{-p_r^2/2mkT} \epsilon^{-p_\phi^2/2mkT}}{\int_{-\infty}^{\infty} dp_\phi \int_{-\infty}^{\infty} dp_r \epsilon^{-p_r^2/2mkT} \epsilon^{-p_\phi^2/2mkT}}$$

where the Boltzmann distribution has been assumed and the tangential component of momentum does not contribute. Then

$$\bar{v}_p = \frac{1/m \int_0^{\infty} p_r \epsilon^{-p_r^2/2mkT} dp_r}{2 \int_0^{\infty} \epsilon^{-p_r^2/2mkT} dp_r}$$

$$= \frac{1}{2}\sqrt{\frac{2kT}{m\pi}}$$

hence

$$A = \sqrt{\frac{2\pi kT}{m}} S N_g$$

C. THE DYNAMICS OF THE SYSTEM

Consider an arbitrary distribution of agglomerates on the surface. Let

$\langle S^2 \rangle$ = the average square radius of the agglomerates

and

$<S>$ = the average radius of the agglomerates.

Then, from conservation of particle number, the equation

$$\frac{dN_g}{dt} = D_s<S^2> e - D_s <S> a N_g$$

can be written, where

$$e = 1.71 \times 10^{12} \epsilon^{-E_b/kT}$$

and

$$a = \sqrt{\frac{2\pi kT}{m}}$$

as derived in parts A and B, and where D_s is the average number of grains per unit area. The equation is simply a statement of conservation of number of atoms.

Consider the process whereby a sample, initially at a very low temperature, is suddenly brought to a temperature sufficiently high that emission is significant. This amounts to the boundary condition that at $t = 0$, $N_g = 0$. Then

$$\dot{N}_g + (D_s <S> a) N_g = D_s e <S^2>$$

has the solution

$$N_g = N_{g_o} (1 - \exp(-D_s a <S> t))$$

where

$$N_{g_o} = \frac{e <S^2>}{a <S>} \quad \text{and } t \text{ is time}$$

Note that once the surface density of the gas reaches its steady value, N_{g_o}

$$E = D_s e <S^2>$$

$$A = D_s a <S> N_{g_o} = D_s e <S^2> = E$$

so that the steady value increases to the situation in which the emission rate equals the absorption rate. Further considerations are impossible without choosing a distribution for the agglomerates.

Let this distribution be

$$D(S) = n_1 \delta(S - S_1) + n_2 \delta(S - S_2)$$

where n_1 is the number of grains of radius S_1 per unit area, and n_2 is the same number for S_2. Assume that $S_1 < S_2$. Then

$$\langle S^2 \rangle = \frac{\int_0^\infty S^2 D(S)\, dS}{\int_0^\infty D(S)\, dS}$$

$$= \frac{n_1 S_1^{\,2} + n_2 S_2^{\,2}}{n_1 + n_2}$$

and

$$\langle S \rangle = \frac{n_1 S_1 + n_2 S_2}{n_1 + n_2}$$

Thus

$$N_{g_o} = \frac{e}{a} \frac{n_1 S_1^{\,2} + n_2 S_2^{\,2}}{n_1 S_1 + n_2 S_2}$$

where e and a are functions of temperature alone. The function

$$F(S_1, S_2) = \frac{n_1 S_1^{\,2} + n_2 S_2^{\,2}}{n_1 S_1 + n_2 S_2}$$

$$= \frac{S_1^{\,2} + r S_2^{\,2}}{S_1 + r S_2} \qquad \text{where} \quad r = n_2/n_1$$

has some interesting properties which give insight to the agglomerate formation process. A plot is shown in Fig. 12, for which S_2 is held constant, and r is the parameter of the family. Assuming $S_1 < S_2$, the "operating point" for the S_1 agglomerates must lie to the left of the line $S_1 = S_2$. A similar plot for the F-surface intersection with the S_2 plane would show the "operating" point for S_2 somewhere to the right of $S_2 = S_1$. For convenience, only one plot need be used as shown in Fig. 12. The reason that the indicated points are operating points is that, for a given ratio r, the rate of emission must equal the rate of absorption once the gas is formed. This condition is always

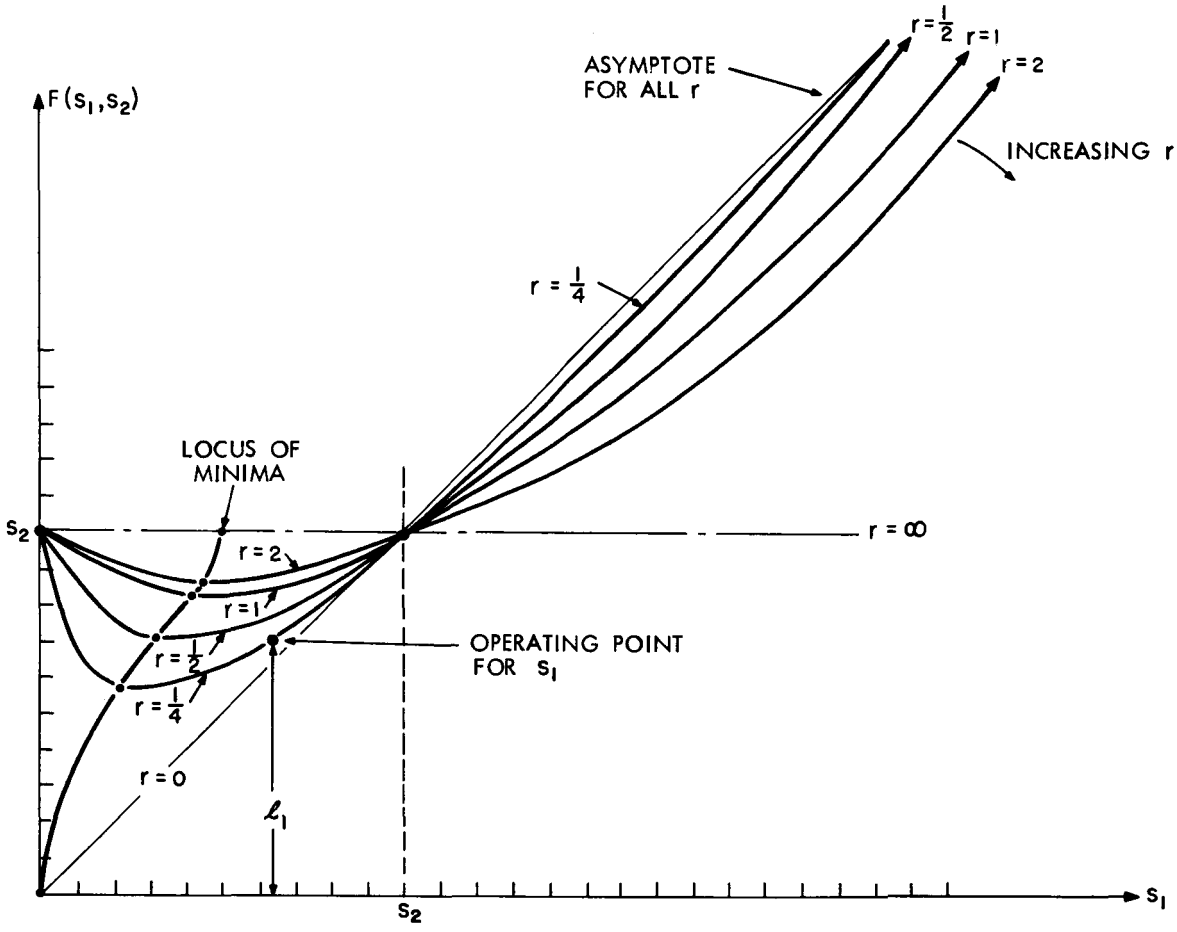

Fig. 12 Plot of the function $F(s_1,s_2)$

true when the surface density of the gas is specified by[7]

$$N_g = N_{g_o} = \frac{e}{a} F(S_1, S_2)$$

Hence, S_1 and S_2 must lie on lines which satisfy this condition for a given "occupation" ratio r. Now define equilibrium as that situation in which the system, no matter how long it is left alone, will not change. Hence, for equilibrium, N_{g_o} must be stationary with respect to fluctuations in the distribution of sizes.

This treatment can give no better definition of equilibrium due to the lack of thermodynamic constraints. For example, it is well known

[7] Note that the time-constant for gas formation is of order 10^{-9} seconds.

that in a phase transition such as this (P constant, T constant) the state assumed by the system is always that which minimizes the Gibbs potential. But, due to the lack of a definition for volume, the Gibbs potential cannot be defined and the information it provides is lost. Note that it would be possible to find another constraint within the framework of this treatment. For example, an energy balance equation could be written which relates the rate of energy increase from absorption to the rate of energy loss through emission. Thermal equilibrium for the agglomerates could be then defined by requiring that these rates be equal. The approximations required to model conservation of energy, however, would be many times worse than those required for the conservation of mass, as above, and such a study was not attempted.

The only way for N_{g_o} to be distribution-independent is for mass to be conserved on the surface, independently of mass of the gas. Thus,

$$\frac{2\pi p}{3}\left[n_1 S_1^{\,3} + n_2 S_2^{\,3}\right] = \frac{\text{const}}{\text{unit area}}$$

Or, equivalently, representing the constant in a convenient way

$$n_1 S_1^{\,3} + n_2 S_2^{\,3} = (n_1 + n_2)\, S_0^{\,3}$$

where S_0 is constant. How, note that any S_1, S_2 satisfying the above relation makes $F(S_1, S_2) = S_0$. This can be proved by observing that $F(S_1, S_2)$ is certainly independent of the values of S_1 and S_2, since the constraint says that the number of atoms in agglomerates on the surface is constant. Any changes in the grain size satisfying this constraint cannot affect N_{g_o}. But $N_{g_o} = \frac{e}{a} F$. Hence, for all values of S_1 and S_2, $F(S_1, S_2)$ has the same value. That this value is S_0 can be shown by picking any values for S_1 and S_2 and finding $F(S_1, S_2)$. For example,

$$n_1 S_1^{\,3} + n_2 S_2^{\,3} = (n_1 + n_2)\, S_0^{\,3}$$

or

$$(S_0^{\,3} - S_1^{\,3}) = r(S_2^{\,3} - S_0^{\,3})$$

Let

$$S_1 = 3^{1/3}\, S_0, \quad r = 3$$

then

$$S_2 = 3^{-1/3} S_0$$

then calculating $F(S_1, S_2)$,

$$F = \frac{S_1^2 + rS_2^2}{S_1 + rS_2}$$

$$= \frac{3^{2/3} + 3(3^{-2/3})}{3^{1/3} + 3(3^{-1/3})} S_0$$

$$= S_0$$

So $F(S_1, S_2) = S_0$ for any S_1, S_2 satisfying

$$(S_0^3 - S_1^3) = r(S_2^3 - S_0^3)$$

Then, as far as the surface density of the gas is concerned, the agglomerates are behaving exactly as if they were all of uniform size S_0. Once the distribution satisfies this constraint, it is stable, since there will be no mechanism provided by which it can change.

The simple process treated here, while not very physical, does exhibit the fundamental feature of the annealing process when described by the gas model: for a given temperature of the substrate, there exists a distribution of agglomerates on the surface which will not change once it is reached. In particular, if the deposition of the agglomerates should happen to provide a distribution for which all agglomerates are of about the same size, annealing will not change this situation.

On the other hand, if the deposition (at a very high rate and low temperature of the substrate) provides a solid layer, annealing will cause it to break up. This phenomenon is not within the realm of the two-member distribution, and is discussed below and in the next section.

D. THE EVAPORATION PROCESS

The evaporation process can be considered as a "superposition" of two gases, the first produced by emission from agglomerates on the surface, and the second produced by the evaporating source. The

emitted gas satisfies the dynamics outlined above, but the gas from the source is comprised largely of atoms with momenta directed normal to the substrate. Hence, if the rate of production of atoms from the source is very much greater than the rate of emission from agglomerates, the criterion for equilibrium discussed above is meaningless.

The rate of surface gas generation due to the source can be calculated from the fact that a typical deposition time for the samples of Section II is 30 minutes for a 20 $\mu g/cm^2$ surface mass density. This corresponds to an arrival rate of 66 atoms per second in a unit area 2500 Å on a side. Now the rate of gas generation due to emission is a function of agglomerate size. Assuming a substrate temperature of 277°C, a mid-deposition grain size of 125 Å (grain radius 62.5 Å), and that there are 60 such grains in the 2500 Å square unit area, emission can typically produce 2.3 atoms per second. Near the end of deposition when the grain radius is up to 125 Å, emission produces about 42 atoms per second per unit area. Hence, at the low deposition rates and high temperatures considered here it would not be invalid to assume that emission from agglomerates is an important process during deposition.

Now suppose that a uniformly thick solid layer forms over the unit area under consideration at some point during deposition. This structure has enormous surface area parallel to the substrate, and, at the temperatures considered, it produces 3600 atoms per second all of which are moving away from the substrate. The structure absorbs only 66 atoms per second from the source. It is clear that this structure would not last long -- in fact, depending on its thickness, it would vanish completely in about an hour.[8]

What would actually happen to the structure, however, is that, due to various preferred orientations of the crystallites comprising it, certain areas would vanish sooner than others, and the amount of area parallel to the substrate would decrease rapidly. This would be accompanied by the occurrence of significant area perpendicular to the substrate,

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[8] These considerations may have an important bearing on CdS film formation. In CdS depositions, the gas evolution rate from the source is a decreasing function of time. At some point during deposition, emission from the substrate may be matched to the source evolution such that conditions are optimal for epitaxy. This may be the criterion for the formation of Type II (very crystalline) CdS surfaces.

and the over-all tendency would be one of unstable large grains breaking up into stable smaller grains. This process is illustrated in greater detail in the next section.

Once large grains have broken up into smaller ones, they are able to absorb atoms from both the source and the gas due to emission, and the distribution of agglomerates remains stable.

It is seen, then, that for a given substrate temperature, there is a critical deposition rate below which a solid layer is not stable. Such rates are those which are exceeded by the rate of gaseous emission from the solid layer surface. A very sensitive measure of the atomic emissivity of gold crystals would be to find this critical rate as a function of substrate temperature.

Note that in annealing, where the deposition rate is zero, any substrate temperature is sufficient to make a solid layer unstable. The only criterion for this case is that the temperature be high enough to cause the breakup of the layer in a reasonable length of time.

V. ANNEALED GRID-LIKE STRUCTURES

An important consequence of the existence of an equilibrium size for gold agglomerates is that solid layer structures are unstable at high substrate temperatures. If a solid layer structure is first deposited on the surface, and then the temperature of the substrate is raised to a level where emission becomes significant, the eventual result will be a completely discontinuous distribution of agglomerates.

A set of samples was made to test this conclusion. The results of the investigation are presented first, and then discussed in terms of the gas model.

A. EXPERIMENTAL PROCEDURES AND RESULTS

The samples for this investigation were all deposited on Type II CdS because preliminary tests showed that the results were not visibly affected by the CdS surface type. Surface mass densities from 10 to 17.5 $\mu g/cm^2$ were deposited onto the CdS-coated substrate at a source temperature of 1510°C. The deposition rate was typically 0.9 Å per second, corresponding to an atomic arrival rate at the sample of 3.4×10^5 atoms per second in a square 2500 Å on a side. The typical temperature of the substrate during deposition was 36°C., as it was heated only by radiation from the source. At this surface temperature, the emission rate is negligibly small, and the criterion for stability of a solid layer is well satisfied. That this is indeed the case is shown in Fig. 13 which shows a 15 $\mu g/cm^2$ solid layer produced under these conditions.

The samples were then annealed in vacuum by raising the temperature of the substrate as quickly as possible to 425°C. This temperature was attained in about 3 minutes. Electrical contact to the structure under investigation was made in the same way as for the voltage formation experiments. The resistance of the structure was monitored throughout deposition and annealing using a sensitive ohm meter. The voltage applied to the sample by the meter was 1.5 volts.

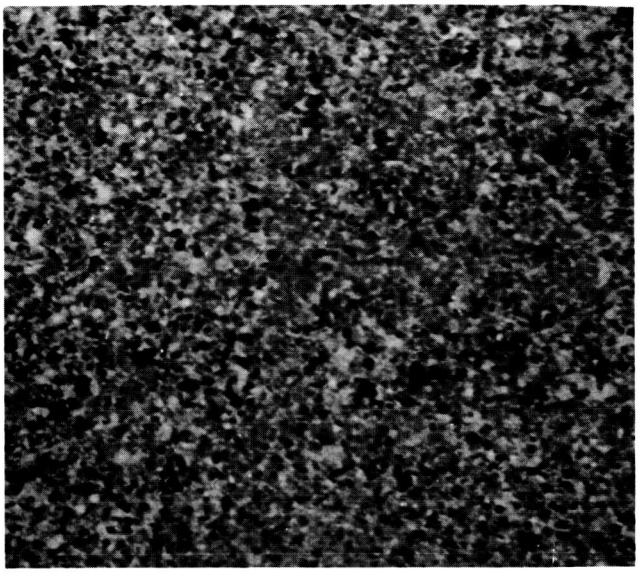

Fig. 13 15 $\mu g/cm^2$ gold solid layer. Average size of crystallites 200 Å. Direct replica, 80,000x.

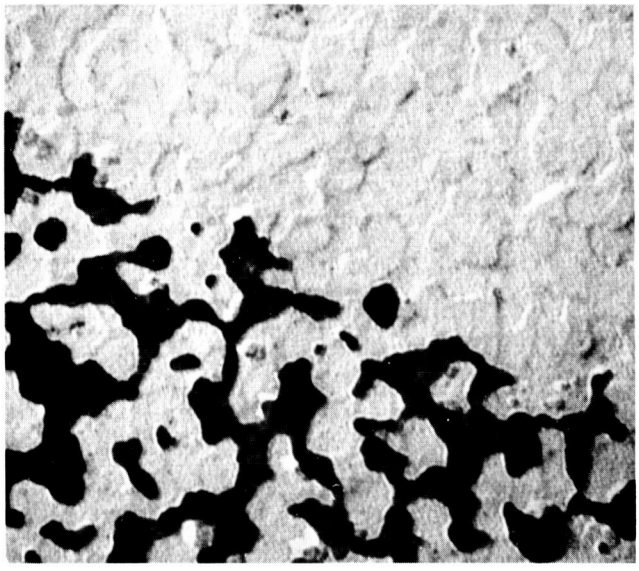

Fig. 14 10 $\mu g/cm^2$ electrically discontinuous structure, Sheet resistance $6 \times 10^6 \Omega$/sq. 80,000x.

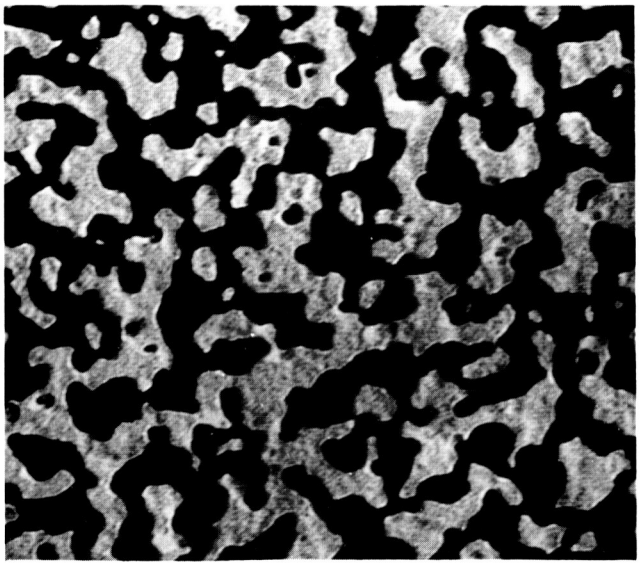

Fig. 15 12.5 $\mu g/cm^2$ grid annealed for 5 minutes. Sheet resistance 54Ω/sq., fraction of open area 0.435. Combination replica, 80,000x.

The effect of this voltage was gauged by comparing a monitored patch of gold with one which was annealed without any meter contacting it. The amount of open area in the monitored structure was found to be measurably less, but in the interest of better control, the process was standardized using the 1.5 volt ohm meter.

The sheet resistance of the structure during the annealing process was a good indicator of what was happening on the surface. For a period of about 2 minutes from the start of heating the substrate, the resistance decreased slowly to a value typically two-thirds of its initial value. This was probably due primarily to a general removal of dislocations and enlargement of crystallite size in the gold structure. After this period, the vacancies forming in the structure began increasing its sheet resistance, and this increase continued for the remainder of the heating cycle. When the sample was cooled, the resistance decreased markedly, possibly indicating a recondensation of the surface gas. This decrease is further discussed below.

Two separate groups of samples were made, one of which was annealed 5 to 7 minutes, while for the other, annealing was allowed to progress for 15 to 20 minutes.

The electron microscopic specimens prepared from these samples were not stripped in acid in order to maintain the integrity of measurements made on their fraction of open area. The annealing process seems to "toughen" the CdS so that a replica of the structural gold can be removed only slowly from the substrate, even in acid. A long exposure to the acid stripping bath might well have removed significant amounts of gold from the replicas, as described in Section II of this report. To avoid this problem, the replicas were stripped in water, a process which required about 2 hours to produce enough replica for an examination of a sample. It was necessary, however, to remove the CdS from the replica with acid, a procedure which required exposure of the replica to HCl for less than a minute.

Micrographs of these samples are shown in Figs. 14-22. The relevant parameters for each of the structures are summarized in Table 3. This data can be used as a catalogue of evaporation parameters for grid-like structures, and is useful for future device work.

Table 3

Surface Mass Density	Sheet Resistance Before Annealing	Duration of Annealing (425°C)	Sheet Resistance After Annealing	Average Aperature Size	Fractional Open Area	Micrograph
10	28	5	∞ *	---	---	Fig. 14
12.5	23	5	54.3	1750	0.435	Figs. 15, 16
12.5	23	10	775	2500	0.640	Fig. 17
15	12.4	5	14.3	2500	0.162	Fig. 18
15	12.4	15	52	2500	0.400	Fig. 19
17.5	11	5	12.9	2500	0.324	Fig. 20
17.5	11	15	18.6	5000	0.414	Fig. 21
($\mu g / cm^2$)	(Ω/sq.)	(min.)	(Ω/sq.)	(Å)		

* 6.2×10^6 Ω/sq.

Note that the annealing process has an increasingly limited effect on the grid-like nature of the structure: the higher the surface mass density, the smaller the apertures and the smaller the fraction of open area, for a given annealing time. There is one important exception to this rule in the sample of Fig. 18, in that the amount of open area is anomalously small. This fact suggests that, in spite of the strict controls maintained on source temperature, substrate temperature, time of annealing and the nature of the CdS surface, there is some variable in the process which makes it slightly unreproducible. This problem will be investigated in the course of further work.

Figure 14 shows a sample which was made electrically discontinuous by this process. It should be emphasized that the bare area of this figure is simply a "pure" replica of the specimen, prepared by the method discussed in Section II, and has nothing to do with the electrical discontinuity. The pure replica area of this plate shows that the Type II surface has not been disfigured in any way by the forming process. The thickness of the grid structure measured in this figure is about 60 $\mathring{A}$.

Figure 16 is a pure replica of the 12.5 $\mu g/cm^2$ grid of Fig. 15. Note that the boundaries of the holes in this structure are almost perpendicular to the substrate. (The point of the arrow in this figure rests on the replica of an open portion of the grid.) The CdS surface is again unchanged by the formation of the grid. The thickness of the structure is about 100 $\mathring{A}$.

The extent to which these structures penetrate the CdS surface can be estimated from Fig. 19, where, in the open areas of the grid, there are replicas of small grains which have penetrated the surface. Many of these have vanished during processing. Note also that the grid itself casts a very short shadow in places--also indicative of slight penetration.

B. GRID FORMATION AND THE GAS MODEL

The behavior of the sheet resistance during the formation process indicates that "annealing" is really two simultaneous processes--the first an enlargement of the size of the crystallites

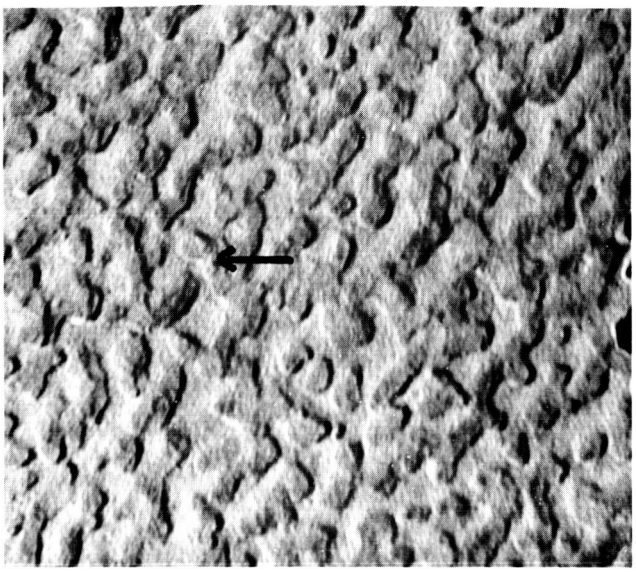

Fig. 16 Pure replica area for sample of Fig. 15. Thickness of grid 100Å. Point of arrow rests on an open area. 80,000×.

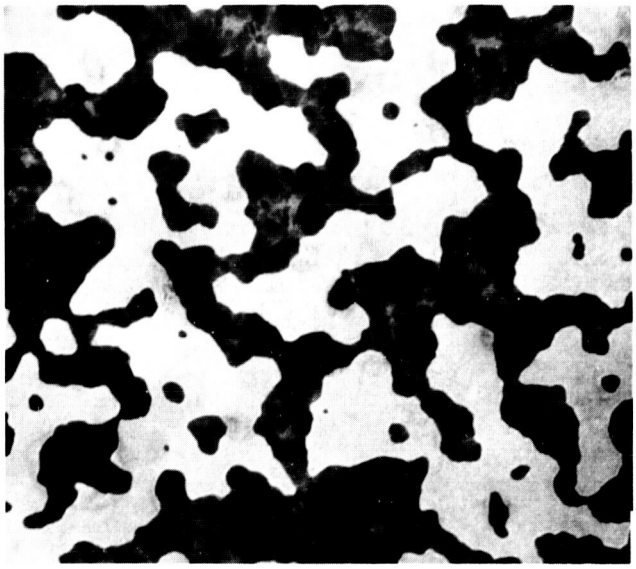

Fig. 17 12.5 $\mu g/cm^2$ grid, annealed 10 minutes. Sheet resistance 775 Ω/sq., fraction of open area 0.640. Direct specimen, 80,000×.

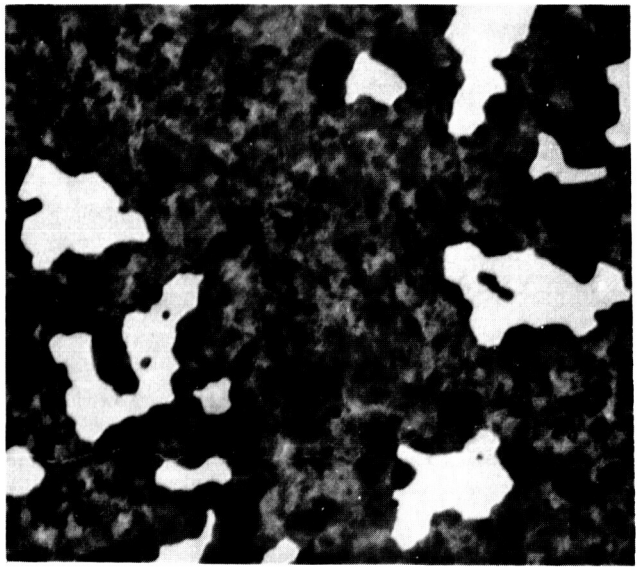

Fig. 18 15 $\mu g/cm^2$ grid, annealed 5 minutes. Sheet resistance 14.3 Ω/sq., fraction of open area 0.162. Direct specimen, 80,000×.

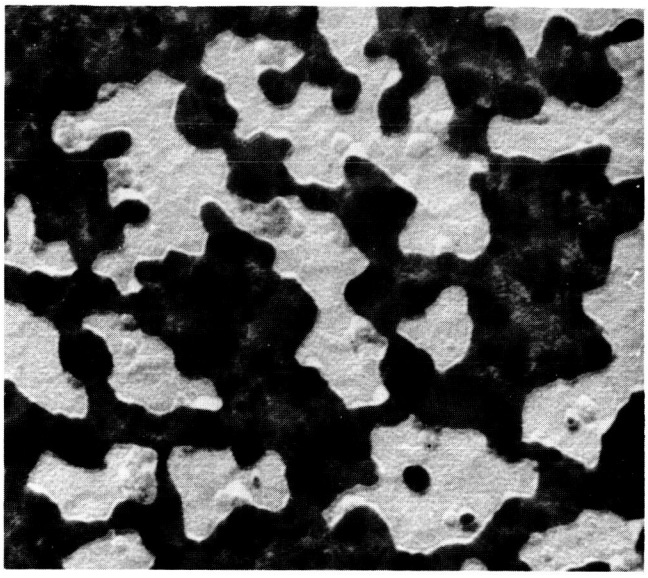

Fig. 19 15 $\mu g/cm^2$ grid, annealed 15 minutes. Sheet resistance 52 Ω/sq., fraction of open area 0.400. Combination replica, 80,000x.

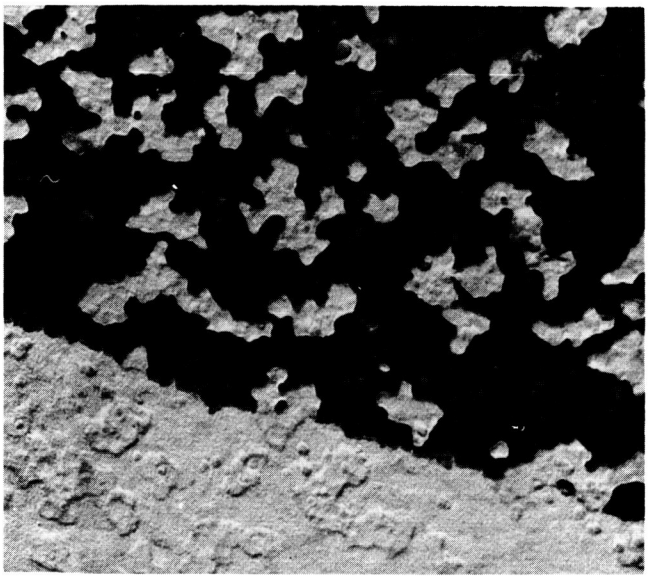

Fig. 20 17.5 $\mu g/cm^2$ grid, annealed 5 minutes. Sheet resistance 12.9 Ω/sq., fraction of open area 0.324. Pure and combination replica, 40,000x.

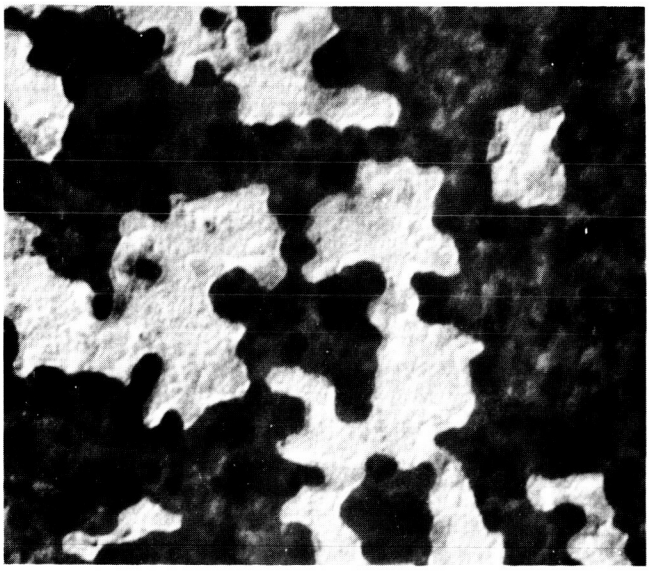

Fig. 21 17.5 $\mu g/cm^2$ grid, annealed 15 minutes. Sheet resistance 18.6 Ω/sq., fraction of open area 0.414. Combination replica, 80,000x.

comprising the gold structure, and the second a formation process through gaseous emission. The crystallite enlargement mechanism can be used to explain why the solid layer does not vanish uniformly over the surface of the sample. Figure 22 shows what might happen.

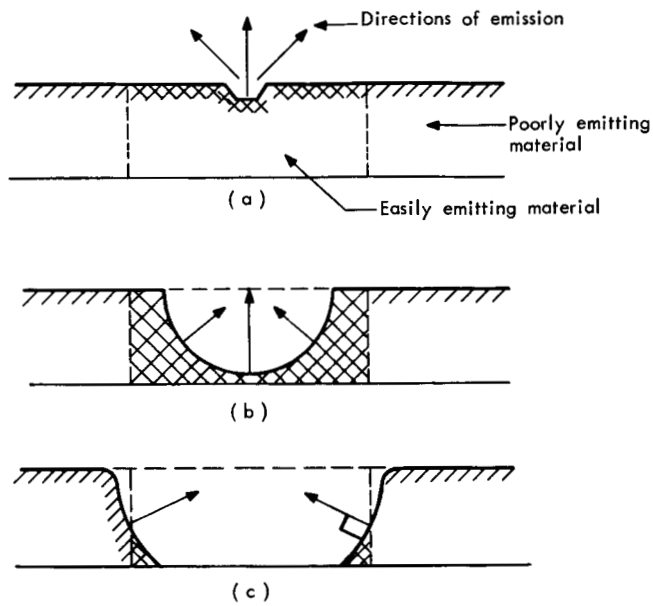

Fig. 22 The grid-formation process

Consider a small area of the solid layer. Certain crystallites on the surface are so oriented that they emit more readily than others, and these begin to vanish, while those remaining behind begin to enlarge. That this does occur is readily seen by comparing the crystallite size in the structure of Fig. 13 (unannealed) with that in, for example, Fig. 18. Hence, poorly emitted areas tend to remain so, while easily emitting areas tend to enlarge in size.

Diagram (b) shows what happens about mid-way through the process. The easily emitting areas are leaving the surface in the directions indicated. Those atoms which leave normal to the substrate are lost from the structure, while those leaving at an angle with the normal may contribute to the surface gas and participate in an absorption process which tends to increase the height of the surrounding poorly emitting structure.

The last stages of the process are illustrated in diagram(c). Here the easily emitting zone has vanished completely (with the possible exception of some small agglomerates which remain behind as poor emitters and begin penetrating into the CdS surface). If at some time during the annealing process a significant number of openings join, the sample becomes electrically discontinuous, as was the case for the sample of Fig. 14. Finally, as the substrate is cooled, the surface gas condenses everywhere on the structure, with a consequent decrease in the sheet resistance of the structure. Note that this very thin, recondensed film can not be seen in any of the open areas of the grids in the figures, probably because it is removed in the HCl cleaning operation. This film may have a detrimental effect on the electrical properties of the structure, especially if it is to be used as the modulator in a field-effect device.

A fairly accurate measurement of the net loss of gold atoms from the substrate can be made from the micrographs. Figures 15 and 16 give sufficient information for this calculation for a 12.5 $\mu g/cm^2$ grid. Consider an area of the substrate 5,000 Å on a side (4 cm. on a side in the micrographs of Fig. 15). Before annealing, the thickness of the solid layer was 76 Å as calculated from Knudsen's law, corresponding to a volume of 1.9×10^9 $Å^3$ of gold in this area. The fraction of open area after annealing can be measured by placing the glass plate micrograph on a piece of fine-grid graph paper and counting "open" squares over a large area. When this is done with 2 or 3 micrographs a very accurate value is obtained. For the sample of Fig. 15, the fraction of open area after annealing is 0.435. The thickness of the grid structure can be measured from the shadow length on the replica of Fig. 16. This thickness is 100 Å. Hence, the volume of gold in this area after annealing is

$$V_g = t_g \, \theta \, A_o$$

where

V_g = the volume of the gold structure after annealing

t_g = the thickness of the grid

θ = the fraction of open area

A_o = the area under consideration

From the data given above, this volume is found to be $1.4 \times 10^{9} \text{Å}^3$, so that the net loss of volume from the sample is $0.49 \times 10^{9} \text{Å}^3$. This corresponds to an average flux of 1.4×10^{3} atoms per second away from the substrate for each such area for the duration of annealing. The total volume moved from the solid layer in the production of open areas is $0.835 \times 10^{9} \text{Å}^3$, and 59 percent of this volume is lost, the rest contributing to the increase in thickness of the structural gold.

The flux of atoms obtained from this calculation would, of course, be higher than that for a surface gas-equilibrium with agglomerates, primarily because here the initially emitting areas are all directed upwards.

C. THE THIN FILM GRID AS A DEVICE ELEMENT

Several exploratory devices were fabricated to investigate the electrical properties of grids as device elements. The results, while not completely successful, were encouraging.

The first few of these devices were simple CdS diodes, the top electrode of which was an annealed grid-like structure. No blocking contact was ever made to the CdS by a grid unless the bare CdS surface was first reated with an oxygen discharge, and then heated at 325°C. for 30 minutes before depositing the gold grid. This procedure always produced good diodes.

The grid formation characteristics on this treated CdS surface are not yet known, nor has any investigation been made of the nature of the treated surface. This will be a subject for ensuing work.

The rest of the devices were triode structures, in which a grid was sandwiched between two layers of CdS which in turn were sandwiched between two thick (300 Å) gold electrodes. The principal problem with these was the difficulty of having the grid make blocking contact to the CdS which was deposited on top of it. The grid leaks current to the top electrode, more than compensating for the current it retards in the flow from the bottom to top electrode. In spite of this problem some modulation has definitely been observed for small voltages applied to the grid.