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MATERIALS AND METHODS FOR LARGE-AREA SOLAR CELLS

by
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ABSTRACT

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GaAs/InAs/Al foil structures have been grown by oxide transport from the respective compounds. Preliminary studies have been made of the growth from the metallic elements using both halide transport and oxide transport. These latter methods have not yet been perfected. The light transmission of some cuprous selenide films on glass has dropped after a period of several months. It is believed that this is due to a cubic → tetragonal phase change. The fact that this change does not occur in all films shows that stable films can be made. Gold gridded $Cu_{1.8}Se$/GaAs/InAs/5μ Al foil solar cells have been made with an efficiency of 4.3% (for an area of 0.73 cm^2) and a power-to-weight ratio of 135 W/lb. With an etching treatment, such cells (on aluminum foil, with efficiencies in the 3% to 4.5% range) have shown no degradation for periods up to 4 months of shelf life, and one month under load at room ambient.

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SUMMARY

GaAs/InAs/5μ Al foil structures have been grown by oxide transport from the respective compounds. The InAs provides an ohmic contact between the GaAs and the Al foil. The thicknesses of the semiconductor layers is respectively of the order 10μ.

Preliminary studies have been made of the growth of GaAs/InAs/Al foil by the reaction of AsH_3 and the trichlorides formed _in situ_ from the metallic elements. GaAs/Mo has also been grown from Ga transported as the oxide and elemental As. The purpose of these studies was to examine methods which might provide larger area films more easily and at lower cost.

Two types of behavior have been found in cuprous selenide films kept under laboratory ambient for several months. In one type the sheet resistance drops with the transmissivity to light remaining constant. This could lead to an improvement of solar cell performance with time. In the second type, the transmissivity drops, the sheet resistance changing very little. This would lead to cell degradation. There is some evidence that the drop in transmissivity is due to a cubic → tetragonal phase change in the cuprous selenide. The fact that this change does not occur in all films gives hope that the cubic phase can be stabilized.

Attempts to find other barrier forming layers have not been successful.

Gold gridded $Cu_{1.8}Se$/GaAs/InAs/5μ Al foil solar cells have been made with an efficiency of 4.3%, an area of 0.73 cm^2, and a power to weight ratio of 135 W per pound.

Some cells have shown a decline in efficiency over a period of months. This appears to be related to changes in the cuprous selenide; but whether it is due in whole, or only in part, to changes in the cuprous selenide is not known. Other cells on Mo have been stable for months. Cells on Al foil which have been given an etching treatment have shown no degradation on shelf life or under load at room ambient. One cell on Mo was stable for a week under load in vacuum.

I. INTRODUCTION

This report covers the work under Contract NAS 3-6466 for the period December 17, 1964 through December 16, 1965.

There are many reasons for attempting the construction of a thin-film, large-area solar cell for use in satellites. The requirements for power continue to increase and hence the total power supply area must increase. This eventually implies an unfurlable or inflatable array, made preferably with flexible cells. The cells should be thin to minimize their weight. They should be simpler to make and to mount than the present single-crystal silicon and gallium arsenide cells to reduce production and assembly costs.

Eventually, a thin-film, large-area solar cell must be judged on a number of factors. These will include: efficiency, power-to-weight ratio, flexibility, radiation resistance, ruggedness, stability (both on earth and in orbit), and cost to make and assemble. These factors, and trade-offs between them, can only be estimated by making actual solar cells. The general purpose of the present study was to investigate materials and methods for the fabrication of large-area solar cells. A more specific (and probably more realistic) goal of the program is to develop cells with efficiencies above 5%, potential areas of the order one foot square, flexible and with relatively inexpensive production costs. For completeness, we now review very briefly the work prior to the start of the period covered by this report.

Gallium arsenide was chosen for greatest effort as the active semiconductor since, theoretically, its band-gap might be expected to provide an optimum compromise between short-circuit current and open-circuit voltage under solar illumination. Its high optical absorption offered the further potential advantage that only a thin film would be needed to obtain complete absorption of the incident sunlight.

Polycrystalline n-type gallium arsenide films, typically 4 mils thick, have been grown on 1-mil molybdenum sheet. These films were frequently cracked and were variable in their electrical properties. Enough acceptable ones had been made to permit the preliminary evaluation of barrier cells (see below). More recently, polycrystalline n-type gallium arsenide films from 5 to 10 microns thick were made on 1-mil aluminum foil. These films showed a photovoltaic response and were, of course, much lighter than the above-mentioned films on molybdenum.

It was hoped that sputtering would permit the deposition of gallium arsenide films at lower substrate temperatures giving a wider choice of substrates and reducing thermal strains and cracking. All sputtered films showed an anomalously high optical absorption, particularly at energies less than the band-gap; an ill-defined change of absorption at the band edge; and high resistivities.

All attempts to make p-n junctions in the polycrystalline gallium arsenide layers had failed, the current-voltage characteristics showing excessive leakage. This we attributed to rapid impurity diffusion along some defects in the gallium

arsenide films. It was hoped that fast flash evaporation of gallium arsenide would permit the formation of a p-n junction before diffusion could cause short-circuiting. Flash-evaporated films of gallium arsenide showed anomalous optical properties and high resistivity, being in this respect similar to sputtered films of gallium arsenide.

A study of barrier formation by low-temperature processes was started. The techniques of forming the conducting films of cuprous sulphide and cuprous selenide were developed. With cuprous sulphide, the optimum compromise between sheet resistance and optical transparency should yield a cell with a sunlight efficiency of between 2% and 3%. By using cuprous selenide, which gives somewhat better results, and by improving the gridding and perhaps using an anti-reflection coat, it is believed that an efficiency greater than 5% can be achieved in areas of the order of 1 cm^2.

The films on aluminum showed a high resistance when measured through the films to the substrate. Efficiencies of the order of 0.1 percent were achieved in very early studies and power-to-weight ratios greater than 50 W/lb. seemed possible in the near future.

The current-voltage characteristics for cuprous sulphide layers on both single-crystal and polycrystalline films of gallium arsenide were studied in detail. They have the same form as similar metal-to-semiconductor barriers. A forward current at small bias is higher for the polycrystalline case which is why the open-circuit voltage drops off faster at reduced illumination than in the single-crystal cells.

During the course of this work, a new photovoltaic effect was found in some semiconductor films. In this effect, the photovoltage increases as the angle of illumination departs from the normal to the film. Voltages higher than the band-gap were observed. While the effect has potential applications in direction sensors, it does not provide a method for efficient power conversion because of the high resistance of the films.

The barrier-forming techniques mentioned above were applied to cadmium telluride, cadmium sulphide, indium phosphide, silicon, and germanium in some exploratory experiments. The results did not suggest that any of these materials would be better than gallium arsenide in a solar cell.

II. GALLIUM ARSENIDE FILMS

During the past year the GaAs/InAs/Al film structure was developed. It will be recalled that this structure has certain advantages over the GaAs Ge-Sn/Mo film structure. The combined film and Al has a total thickness about one fifth, and a weight-per-unit area of about one tenth that of the film and Mo. In addition, it is more flexible and shock resistant. It is principally for these reasons that the film on Al is now exclusively used in the solar cells.

One characteristic of the film growth process had been low yield and reproducibility of GaAs films suitable for use in solar cells. With pressed-gold contacts, such films must have a series resistance of the order of 30 Ω and a good diode characteristic with a breakdown voltage of at least 3 V. During the past year about 200 films have been grown for various purposes in two furnaces, and from this a pattern has emerged. Whenever a furnace part (such as a graphite heater) had to be replaced, the first dozen or so films with the new heater, had poor diode characteristics. It was found that a high temperature bakeout of a new graphite heater was necessary for the re-establishment of good growth conditions. In general, it was found necessary to run the furnace repeatedly under the same conditions in order to reproduce good quality films. In all the work on the growth of GaAs films by vapor transport, in the furnace arrangement used, only one growth parameter was ever found by which the electrical properties of the film could be partially controlled. Note that the parameters of substrate temperature and growth rate are not included here. It was earlier found that the highest substrate temperature, limited by the melting point of Al ($\sim$ 650°C) was the best temperature for film growth. Also, the range of growth rates, using "dry" hydrogen (0.5 micron per hour) was approximately fixed by the growth process of oxide transport at the temperatures employed. It was found that the hydrogen flow rate could be varied in a manner so as to influence the electrical characteristics of the film in a controlled and reproducible fashion. The average flow rate of hydrogen through the furnace was about 2 cc per minute. When the furnace was operating it was found that:

(1) An increase in the flow rate resulted in a decrease in the series resistance through the film and a decrease in the breakdown voltage.

(2) A decrease in the flow rate resulted in an increase in the series resistance through the film and an increase in the breakdown voltage.

This approximate relationship is plotted in Fig. 1. It is emphasized that this relationship is not a general one, but applies only to our particular furnace geometry and conditions. Furthermore, although we have speculated on the reasons for this dependence, we have no satisfactory explanation for it.

Another observation of the growth process is that the film growth rate decreases with time. The relationship is plotted in Fig. 2. During film growth, a partly transparent whitish deposit builds up on the surface of the source GaAs and it is evident that this deposit tends to retard the growth rate.

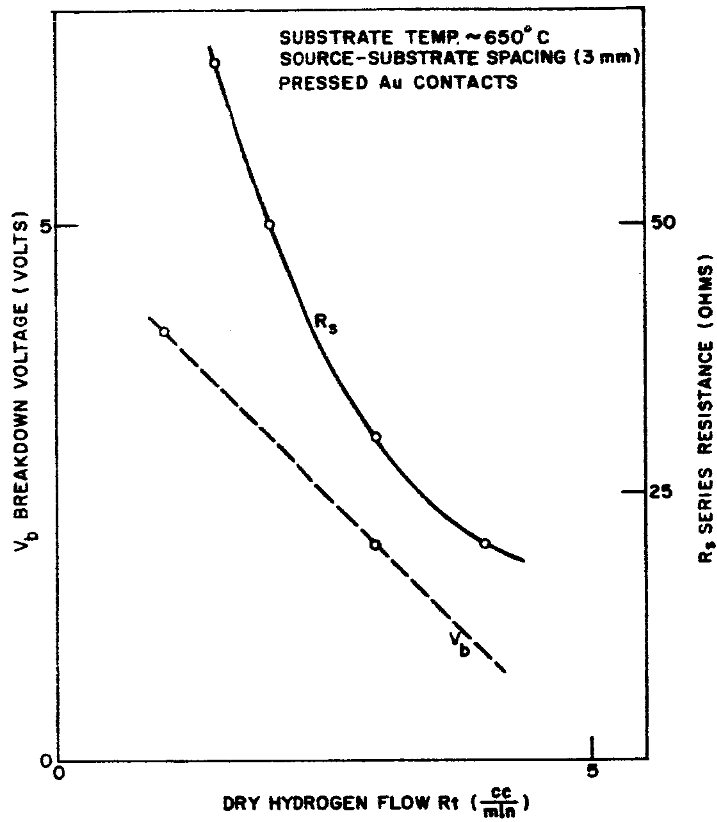


Fig. 1 Effect of hydrogen flow rate on film properties.

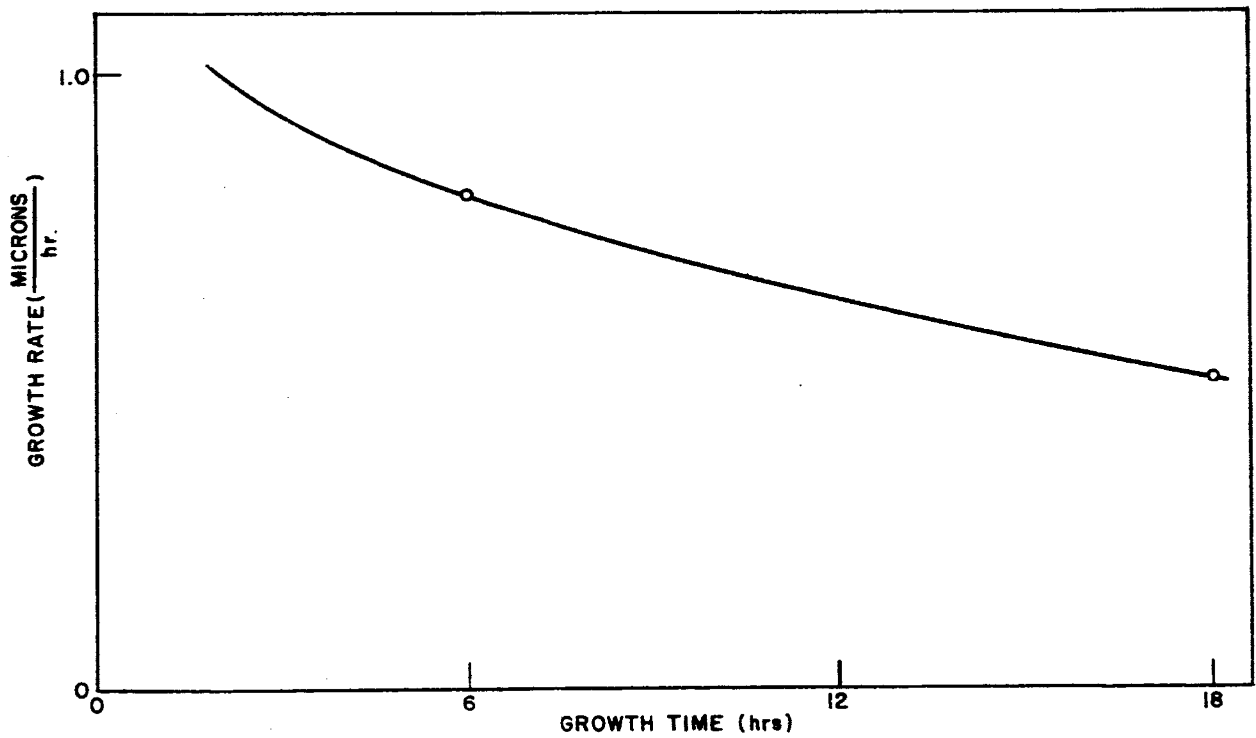


Fig. 2 Change of growth rate with time.

Although we have speculated on the reasons for these phenomena, we have no satisfactory explanation for them. One speculation is that oxides tend to build up on the surface of the GaAs source and even in the crystalline boundaries of the growing film. The formation of these oxides can be retarded with higher hydrogen flow rates which in turn lowers the resistance and breakdown voltages in the films. Therefore, a degree of control over some film parameters was obtained and we are able to grow films and control them within a limited range of the I-V characteristics.

The thicknesses of the InAs and GaAs films have been fixed by the minimum thicknesses necessary for these films to perform their respective functions. The InAs film must form the low resistance contact and a thickness of about 6 microns has been required. The GaAs film must serve as the light absorbing, low leakage depletion region over large areas and a thickness around 12-14 microns is necessary.

The substrate first used was ordinary commercial Al foil 25 microns thick. Two effects occurred in films on this substrate:

(1) Normally the film would "bow" upon heating and cooling, because of differential thermal expansion between it and the GaAs.

(2) Lines could often be seen in the Al after completion of the GaAs film growth which were believed to be microscopic cracks which extended through the GaAs film. When a cell was completed, the cracks divided the cuprous selenide layer into separate, electrically isolated areas.

An investigation was made into the use of thinner aluminum foil substrates. Foil thicknesses of 0.5, 4.5, 6, and 12 microns were tried. The 0.5 micron thick foil could not be handled without crumbling. The 6 and 12 micron thick foil strained the film in a manner similar to the 25 micron thick foil. The use of the 4.5 micron thick foil resulted in an improved structure. The "bowing" that was characteristic upon heating and cooling with the thicker substrate did not occur. The microscopic cracks were eliminated. It was with the use of this foil that the best cells were made.

Another problem then appeared. Close examination of this foil revealed it to have many pinholes of micron dimensions. Five different producers of aluminum foil were contacted. In general, they all agreed that foil under about 12 microns thick could not be made pinhole free because of the nature of the rolling process. One opinion was that dust particles sticking to the foil caused the pinholes when it was rolled. Furthermore, foil of greater than 99.9+ purity could not be rolled so thin because of insufficient tensile strength.

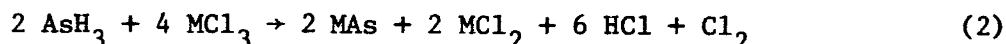
Because of this, a small effort was started for the purpose of making Al foil of the desired specifications. After about one week, we were able to grow thin ($\sim$ 3 micron thick) practically pinhole free foil by vacuum evaporation. Pure aluminum (99.999%) is evaporated from a tungsten spiral to the desired thickness onto a glass slide. The glass slide is treated with a uniformly thin oily film to facilitate removal of the foil from the slide. If care is exercised in keeping the slide "dust" free, the foil contains very few pinholes. We are now using this foil as the substrate for the semiconductor films.

While the oxide-transport method described above has proved convenient for experimental work, it would have a major disadvantage in production. Because it uses the compounds GaAs and InAs either as crystal slices or powder, it would be expensive. It is also slow, the GaAs/InAs/Al structure requiring two sequential 16 hr (overnight) growths. Finally, the close-spaced technique would not be easy to extend to areas as large as one square foot.

An alternative is to use "halide transport". This method has been used elsewhere in these Laboratories and has the potential advantages that elemental Ga and In could be used as the starting materials, that the rate of growth would be higher, and that the technique might be more readily extended to larger areas than one requiring a close space between the source material and the Al substrate. The reactions are:

$$2M + 6HCl \rightarrow 2MCl_3 + 3H_2 \quad (1)$$

where M = In or Ga



$$2\ AsH_3 + 4\ MCl_3 \rightarrow 2\ MAs + 2\ MCl_2 + 6\ HCl + Cl_2 \quad (2)$$

Reaction 1 is carried out at a temperature close to 700°C, and reaction 2 between 600°C and 650°C. The arsine, diluted with hydrogen, is used in excess to avoid the formation of liquid gallium which, if present, leads to whisker growth by the vapor-liquid-solid reaction.

The reaction chamber is shown diagramatically in Fig. 3. For the first stage of growth, hydrogen chloride plus hydrogen is bubbled through the molten indium. To prevent the gallium from reacting, hydrogen is bubbled through it. In the second stage, hydrogen chloride plus hydrogen is bubbled through the gallium and hydrogen through the indium. The gases enter the reaction chamber through jets which serve two purposes: they aid in mixing the metal halide and the arsine, and also isolate from the halide containing atmosphere of the reaction chamber the metal which is not being deposited.

The reaction chamber is surrounded by a wire-wound furnace between the levels F. The Al foil is placed on a re-entrant tube as shown and is adequately cooled since the bottom of the furnace is left open. The fifth tube to enter the furnace permits it to be flushed out with nitrogen at the end of a run.

Initially, some difficulty was experienced with the jets plugging before a run could be completed. This has now been overcome by placing a heater in the position shown by the dotted lines. The immediate remaining difficulty with this technique is to obtain uniform deposits on the Al foil without excessive loss of GaAs to the exit tube. There are also some problems with cracking and curling of the Al foil, but they are not unsolvable.

Another approach to growth from the elements is illustrated in Fig. 4. In this method Ga is transported as the oxide and As is introduced as the vapor by placing As in a cooler part of the furnace. We have demonstrated that the method works in principle. A difficulty with this method is that for efficient transport of the Ga, the Ga to substrate spacing must not be too great, yet the As vapor must be introduced uniformly throughout this volume. Work on this technique has only recently been started.

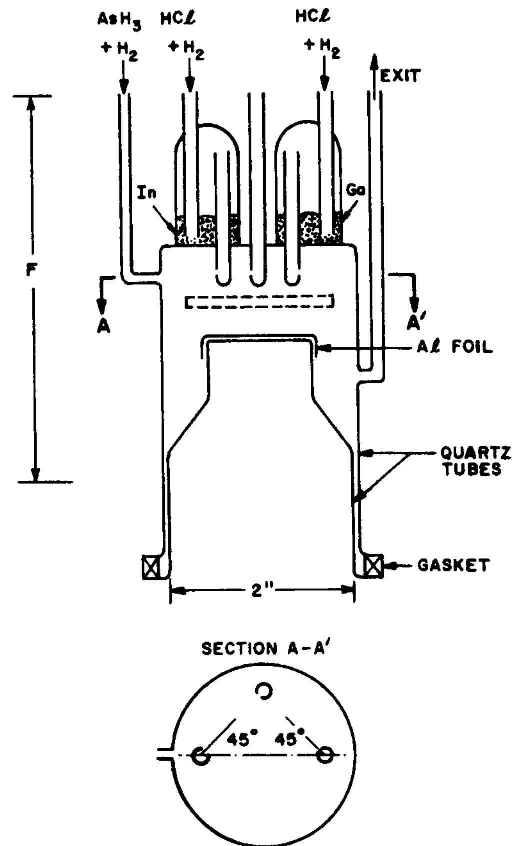


Fig. 3 Halide transport furnace.

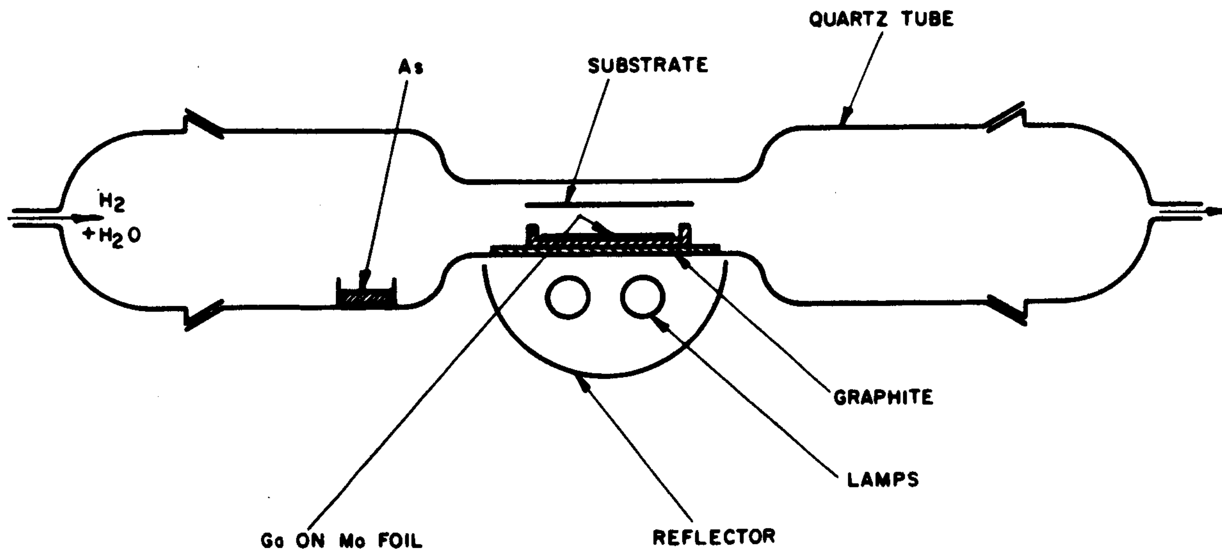


Fig. 4 Growth from elements by oxide transport.

III. CUPROUS SELENIDE FILMS

Cuprous selenide has been used for barrier formation since it provides the best compromise between sheet resistance and light transparency among the barrier-forming materials studied. The films used on a solar cell are typically 70% transmitting to 1.5-eV radiation, have a sheet resistance of the order 70 Ω per square (when evaporated on glass), and are about 220 Å thick.

Thin films present their own complexities, and it will be convenient, therefore, to start by considering the bulk properties of cuprous selenide.

Cuprous selenide can be prepared and stored (in the bulk form) in a range of compositions $Cu_{2-x}Se$, where $0 \leq x < 0.26$. There is evidence that the composition $Cu_{1.8}Se$ is the most stable form and the mineral, berzelianite, is found with compositions close to this value. Hansen[1] has reviewed the crystallographic data. Cuprous selenide exists in two forms: α (cubic) at higher temperatures and β (tetragonal) at low temperatures. It is said that the $\alpha \rightleftharpoons \beta$ transition temperature varies from 110°C to below room temperature as x increases. Earley[2] discusses previous work on this material and gives measurements of the lattice constant of the α form as a function of x. These have been supplemented by work here and the results are shown in Fig. 5. For $x \geq 0.26$ a second phase Cu_3Se_2 (umangite) appears.

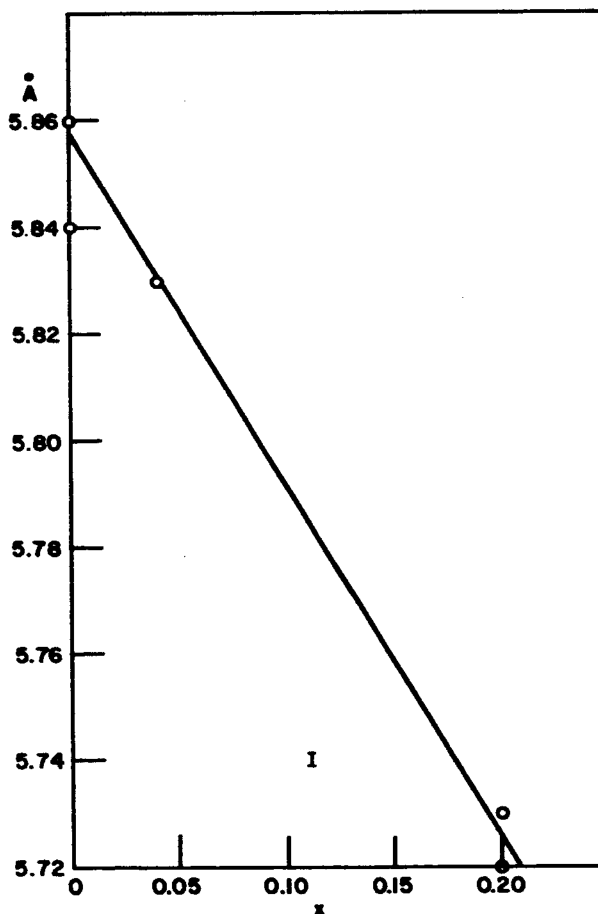


Fig. 5 Lattice constant "a" as a function of stoichiometry factor x for cubic $Cu_{2-x}Se$ from J. W. Earley, Am. Minerologist *35*, 337 (1950) supplemented by work done here.

The electrical properties are explained on the same basis as those of cuprous oxide. The copper vacancies are acceptors and as x increases from zero to 0.2, the specific resistance drops by two orders of magnitude to a value of the order 1.6×10^{-4} Ω-cm. Within limits to be described later the material is stable in room air.

Bulk cuprous selenide can be prepared by melting together weighed quantities of the elements in a sealed evacuated quartz tube. With slow cooling, the charge solidifies into relatively few crystals which show (111) cleavage. This cleavage surface does not tarnish. It has a dark metallic appearance.

We now review some fairly general properties of vacuum deposited thin films, taking metallic copper as an example. Let us suppose that it is being deposited on glass and that when the mean thickness of the deposit is t the resistance per square is R. We define a specific resistance, s, for the deposit by

$$s = Rt \tag{3}$$

Three successive stages can be recognized in the growth of the film:

Stage I: Cu atoms reaching the substrate migrate to and join isolated islands of copper. At this stage s is orders of magnitude larger than the value for bulk copper. The number of islands per cm^2 (typically $\sim 10^{12}$) is a strong function of the pre-treatment of the substrate. It also tends to increase with reduced substrate temperature and increased rate of evaporation.

Stage II: The islands begin to touch and s drops rapidly. The value of t at which this stage is entered is smaller the larger the number of islands per cm^2,

Stage III: The spaces between the islands have been filled in. s approaches an approximately constant value which is still, however, several times larger than the value for bulk copper.

If film growth is stopped in stage II and air is admitted, R rises. This is presumably due to the oxidation of the necks between the islands.

If film growth is stopped in stage III but air is not admitted, R drops. The drop can be accelerated by heating and is presumed to be due to the annealing out of crystal defects, and grain boundary rearrangement in the film.

We shall present evidence below that cuprous selenide films go through the same stages during their growth but that there are added complications due to the effects of nonstoichiometry, the $\alpha \rightleftharpoons \beta$ transition, and in some cases the effect of oxygen.

In the early work, cuprous selenide films were deposited by conventional vacuum evaporation. A progressive loss of selenium from the charge caused successive changes of film composition, and eventually films with excessive resistance. To avoid this difficulty, flash evaporation was then employed.

In order that the film shall have the composition of the charge, both microscopically and macroscopically, two conditions have to be satisfied:

(1) The complete evaporation of one particle should deposit not more than a monolayer at the substrate, for if each particle fractionates and gives a thick layer, then the final film will be stratified (in the absence of sufficient diffusion).

(2) All atoms reaching the substrate (or film) should stick.

Condition (1) is readily satisfied. The particles are seived to pass a 0.297 mm mesh but be stopped by a 0.25 mm mesh. The average particle weight is of the order 20 μgm giving a 0.2-Å deposit at 15 cm.

The second condition is less certain of being satisfied where one of the elements in the compound (Se) has a high vapor pressure. It is shown in Appendix I that if the selenium has a low accommodation coefficient on glass, then during stage I of the film formation a serious departure from the expected composition could occur. There is no evidence for this. In one case a thicker $Cu_{1.8}S$ film was analyzed and found to have the composition of the starting material, but being thicker, the effect discussed in Appendix I would be minimized. Electron Diffraction studies of flash evaporated films show a lattice constant of 5.74 A, indicating a composition close to $Cu_{1.8}Se$.

If T is the transmission to light (in our case 1.5-eV radiation) and α is the coefficient of absorption, then

$$\ln T = - \alpha t \quad (4)$$

Substituting for t from Eq. (3):

$$\ln T = - \frac{\alpha s}{R} \quad (5)$$

The resistances R_M are measured between evaporated gold electrodes 25 mm wide and 9.5 mm apart. The transmissivities are not corrected for reflection.

Figure 6 shows a plot of $\ln T:1000/R_M$ for films made by the flash evaporation of $Cu_{1.85}Se$, under a variety of conditions. With the exception of film 103, which will be discussed later, it can be seen that for five days the resistance drops with time, T remaining nearly constant. This drop in resistance begins with the completion of the evaporation while the specimen is still in vacuuo and continues (without apparent acceleration) in air. It is largely completed in five days. We attribute this drop in resistance to annealing of the film with a consequent increase in mobility.

If a film is made from stoichiometric Cu_2Se, or Cu_2Se containing a slight excess of Cu its initial resistivity is high. It shows the slow changes of resistance described above, but in addition a rapid drop of resistance on the admission of air. Its final resistivity corresponds to a composition close to $Cu_{1.8}Se$. These reactions proceed rapidly and to completion because of rapid Cu diffusion through the high concentration of Cu vacancies.[3] Figure 7 indicates the supposed initial and final states of such a film.

Films containing a greater amount of copper than those of the previous paragraph show an increase in resistivity, and become clearer with oxidation. Cu_2O has been detected in such films by electron diffraction. We believe that

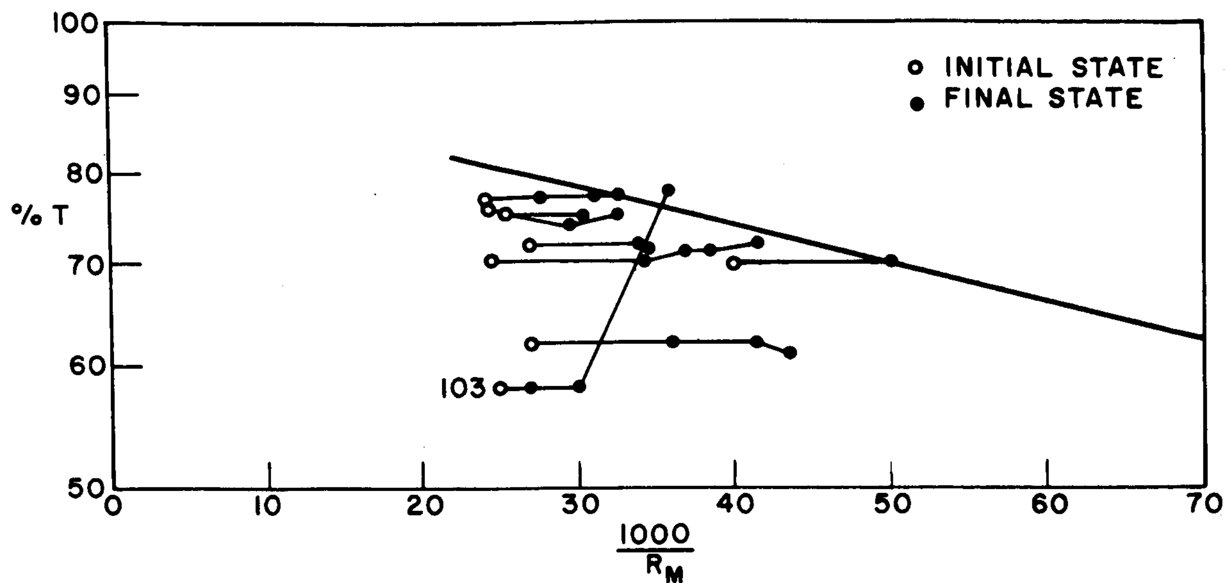


Fig. 6 $\ell nT:1000/R_M$ for $Cu_{1.85}Se$ films.

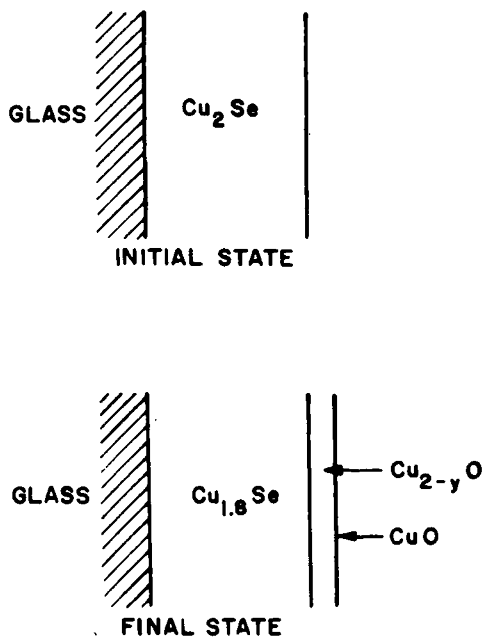


Fig. 7 The oxidation of Cu_2Se films.

the changes in resistance and color are due to the formation of a major amount of Cu_2O in such films.

Finally, some very thin films ($T \approx 80\%$ or less) can show an increase in resistance with time. It seems probable that such films are in stage II of their development.

Figure 8 shows the initial and final states of some films after periods of from 4 to 6 months. Where the resistance has dropped appreciably, it may have dropped in the first few days after film formation. There appear to be two extreme types of behavior:

(1) A drop in R by about 50% with little change in T.

(2) A drop in T to about 2/3 rds of its initial value with little change in R.

Behavior of type (1) is encouraging since it would lead to an increase of solar cell efficiency (provided, of course, that the barrier height is maintained). Behavior of type (2) would lead to cell degradation.

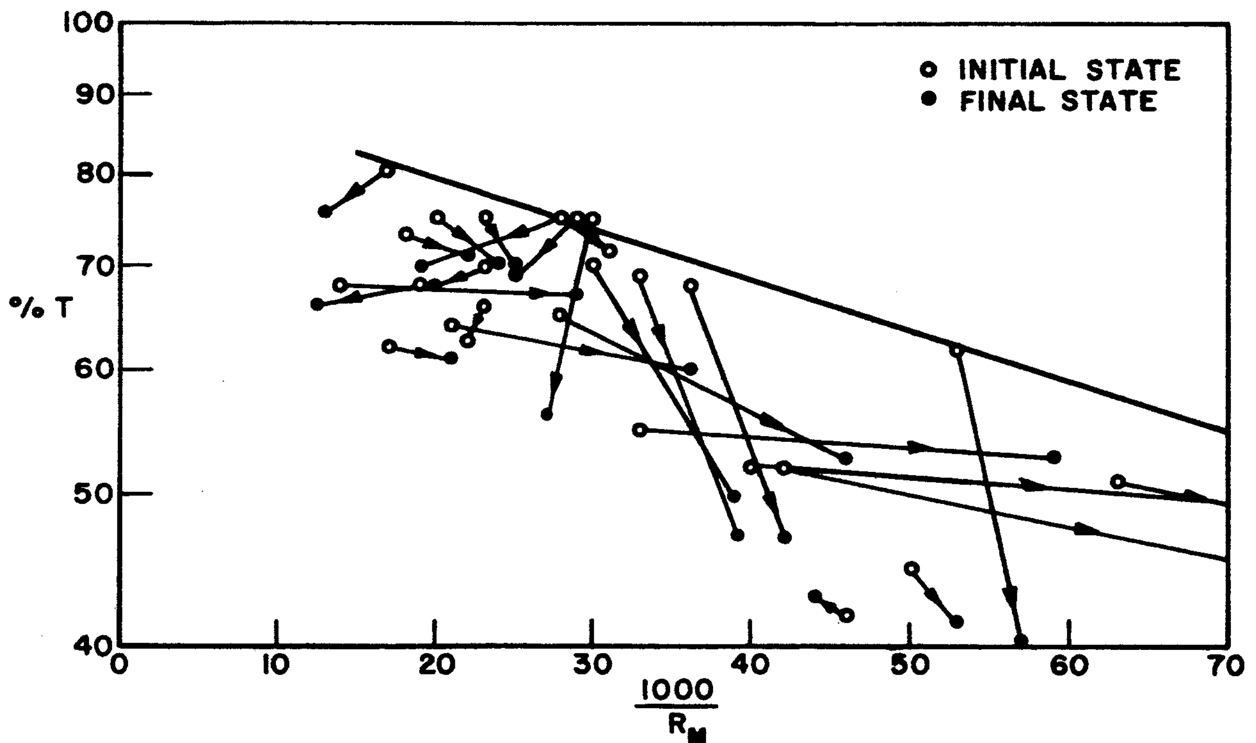


Fig. 8 Initial and final states of cuprous selenide films.

When the change in T occurs, the film which was orange by transmitted light becomes pale blue, and of course its transmission spectrum is changed, as shown in Fig. 9. This change and the relative constancy of the resistance are difficult to explain by any plausible changes in mobility or carrier concentration. The film which had been optically isotropic under the polarizing microscope is now anisotropic and hence presumably noncubic. The previous state of color and transmissivity can be restored by heating in air to a temperature in the range 110° to 170°C.

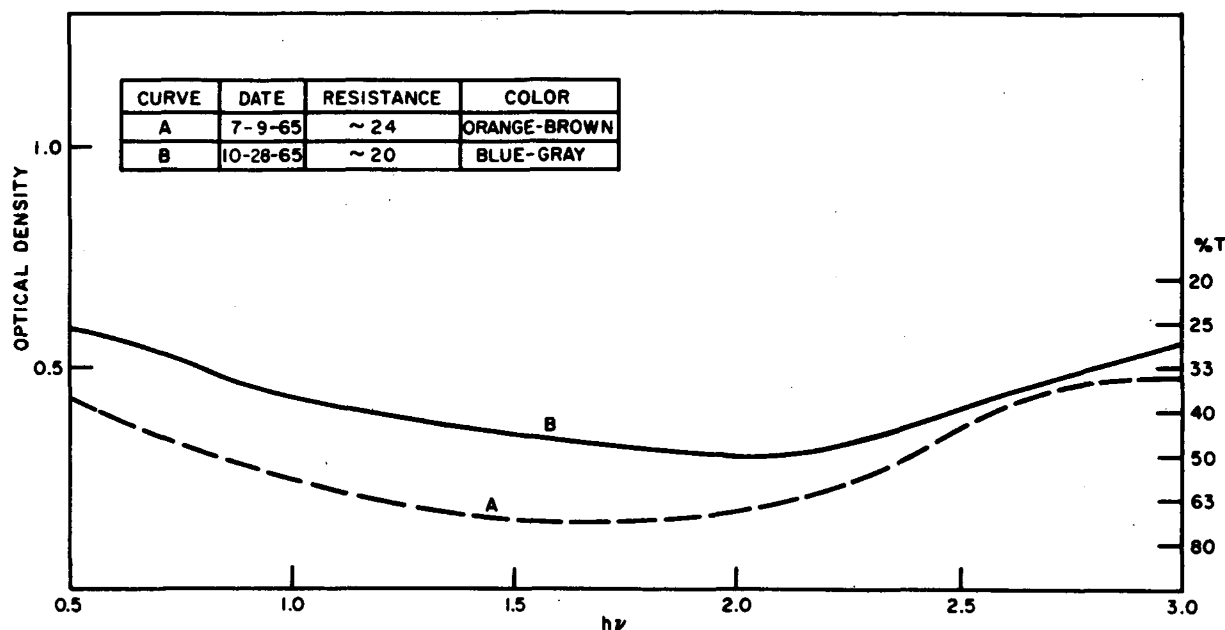


Fig. 9 Optical absorption spectra of cuprous selenide on glass.

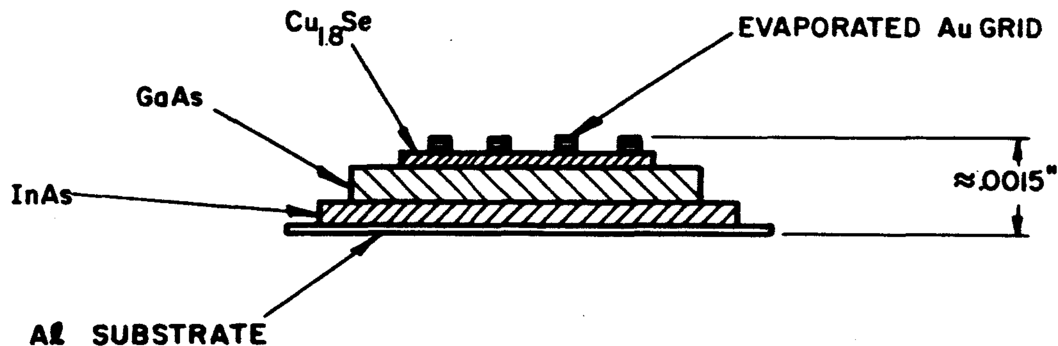
These observations have led us to believe that the drop in T is due to an α (or cubic) $\rightarrow\beta$ (tetragonal) phase change in the film.

To date, we have been unable to get a piece of the 'blue' film in a form suitable for electron diffraction studies.

It may be significant that film 103 of Fig. 6 formed with a lower boat temperature and possibly selenium deficient looked blue on deposition. After heating to 175°C for 15 minutes, it became brown and T increased as shown. Beyond the hint that the stoichiometry may control the $\alpha \rightarrow \beta$ transition temperature, we have no guide as to what differentiates type (1) and (2) films in their preparation. The transition, when it occurs, is very sluggish, spreading patchily across the film in a matter of weeks.

IV. SOLAR CELLS

Figure 10 shows schematically the structure of the solar cell. The GaAs film is first etched with 1% bromine-alcohol prior to the flash evaporation of the barrier layer. The cuprous selenide film is typically 200 Å thick and 70% transmitting at 1.5 eV. The specific resistivity in these films is of the order of 10^{-4} Ω-cm. A "comb" shaped gold grid is then evaporated in order to lower the cell resistance. In some cases an anti-reflection coating has been added. The Al foil is of the order of 4 microns thick, the InAs layer around 10 microns and the GaAs film about 15 microns thick. The completed cell is approximately 1.4 mils thick.



$Cu_{1.8}Se$ – GaAs CELL WITH Aℓ SUBSTRATE

Fig. 10 Surface barrier cell structures.

With Pt/GaAs film solar cells the spectral response peaks close to the band-edge and remains almost constant out to 3.0 eV. This, and the short-circuit current density, is due to the fact that the barrier is at the surface of the GaAs and the Pt acts as a neutral filter.

By comparison, the spectral response of $Cu_{1.8}Se$/GaAs/Mo film cells is anomalous. It is about 60% of the maximum at the band-edge and increases steadily to peak broadly at 2.2 - 2.4 eV. The transmission of the selenide is constant from the band-edge to 2.0 eV and drops slowly, so that light absorption in the selenide does not provide an explanation.

It is possible, but not proven, that the cuprous selenide layer is acting as a better anti-reflection coating at 2.3 eV than at the band-edge. If this is so, an anti-reflection coating designed to work at 1.6 eV could give a marked improvement in cell performance. The fact that the selenide acts in some degree as an anti-reflection coat is indicated by the high, short, current density achieved with these cells, and by its visual appearance when evaporated onto the GaAs.

Figure 11 illustrates a similar but not identical behavior for a cell on Al foil. Cuprous selenide was simultaneously evaporated onto the GaAs and onto glass. Curve "a" gives the response per incident photon, curve "b" shows the variation in percent transmission for the selenide film on glass. Curve "c", the response per photon absorbed in the GaAs as calculated on the assumption that the only effect of the selenide film is to absorb radiation and that reflection corrections are small. The curve "c" is normalized to the same peak value.

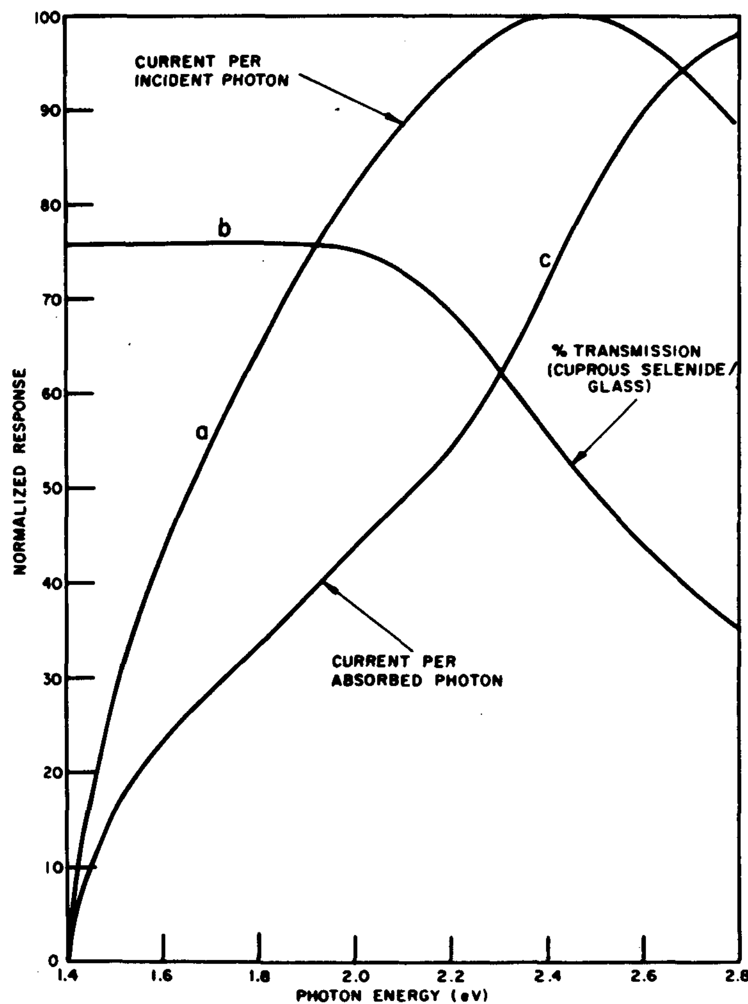
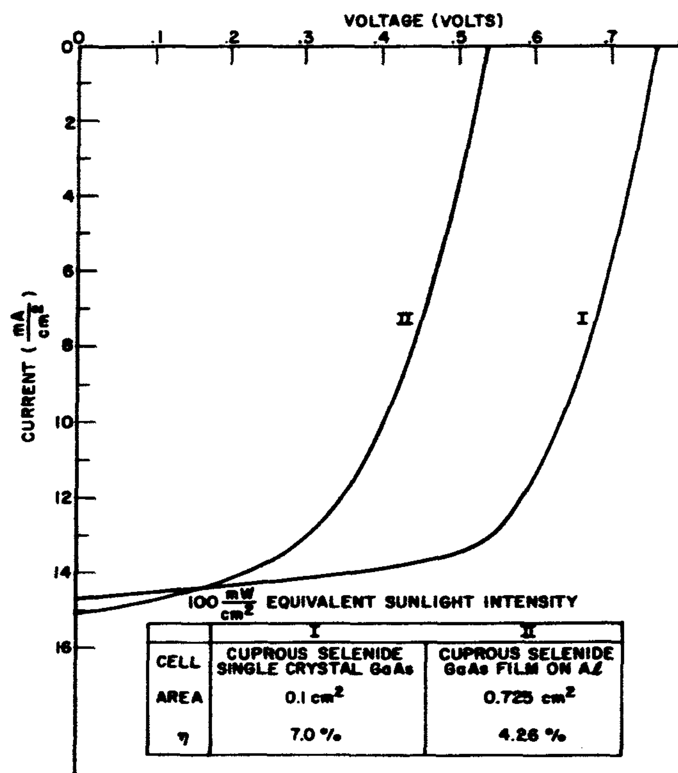


Fig. 11 Spectral response for $Cu_{1.8}Se$/GaAs film cell.

Measurements of cell efficiency have been made as follows: The incident light intensity and short-circuit current are first measured in sunlight. The short-circuit current corresponding to 100 mW/cm^2 incident intensity is then calculated by assuming I_{sc} to be proportional to incident intensity. This current is then reproduced in the laboratory under tungsten illumination and the complete I-V curve is obtained. The assumption of linearity is more justified as the extrapolation becomes smaller. This method also requires that the cell is not limited by series resistance.

Figure 12 shows the I-V characteristic under illumination for a cuprous selenide GaAs barrier on Al foil. The shape of the I-V curve makes evident the present limitations imposed by series and sheet resistance. The efficiency of 4.26% is calculated without subtracting the gridded area. By weighing the cell, a power-to-weight ratio of 135 W/lb. was measured. The current density obtained with this cell, 15 mA/cm^2 can be compared with 17 mA/cm^2 for a GaAs single crystal p-n junction cell.



	I	II
CELL	CUPROUS SELENIDE SINGLE CRYSTAL GaAs	CUPROUS SELENIDE GaAs FILM ON Al
AREA	0.1 cm^2	0.725 cm^2
η	7.0 %	4.26 %

Fig. 12 Comparison of I-V characteristics for single crystal and film cells.

Barriers of cuprous selenide to single crystal GaAs have been formed and fabricated into cells. The I-V under tungsten illumination (set for 100 mW/cm^2) is shown in Fig. 12. The V_{oc} is 0.76 V and I_{sc} is 15 mA/cm^2. The efficiency

is 7%. Besides some difference in series and sheet resistance, the main limitation in the thin film cell is the V_{oc} which is 30% lower than the single crystal cell.

Stability

The characteristics of solar cells made with cuprous selenide-GaAs barriers on aluminum have been checked for several months. These cells had degraded noticeably after several days. An apparent increase in series resistance accompanied by a gradual discoloration of the cuprous selenide film was observed. As stated earlier, color changes have been observed in cuprous selenide films on glass but the resistance increase cannot be attributed solely to the cuprous selenide film because no such unambiguous resistance increase occurred in the films on glass. However, it should be noted that the resistance is measured along the film, on glass and through the film in the cell under dark conditions. The increase in series resistance of the cell was not caused by changes in the GaAs film or the GaAs-aluminum contacts, as these could be checked separately.

Degraded cells on aluminum can be restored to their original characteristics by etching them in 1% nitric acid. A cell thus treated has greatly improved stability characteristics.

It has been noted that cells on molybdenum substrates are stable for periods over a month in room ambient. These cells have not been etched and have no protective coating. After this period, a very slow deterioration may occur. Similar observations have been made on cuprous selenide to single crystal GaAs barriers. In all cases, the deterioration is accompanied by the characteristic discoloration of the cuprous selenide.

Figure 13 shows an example for etched cells. The results for an unetched cell on Mo is also plotted under periodic and continuous load testing. Cells can also be stabilized by etching them immediately after they are fabricated. It has been found that an alternate method of restoring cells is to heat treat them in vacuum at about 150°C for an hour. These treatments result in the restoration of the original color of the cuprous selenide film as well as the original performance of the solar cell. In view of the evidence presented in section on cuprous selenide films it appears as though cell degradation can occur by means of changes in the cuprous selenide film. These changes result in lowered optical transmission and increased resistance through the cuprous selenide-gallium arsenide barrier.

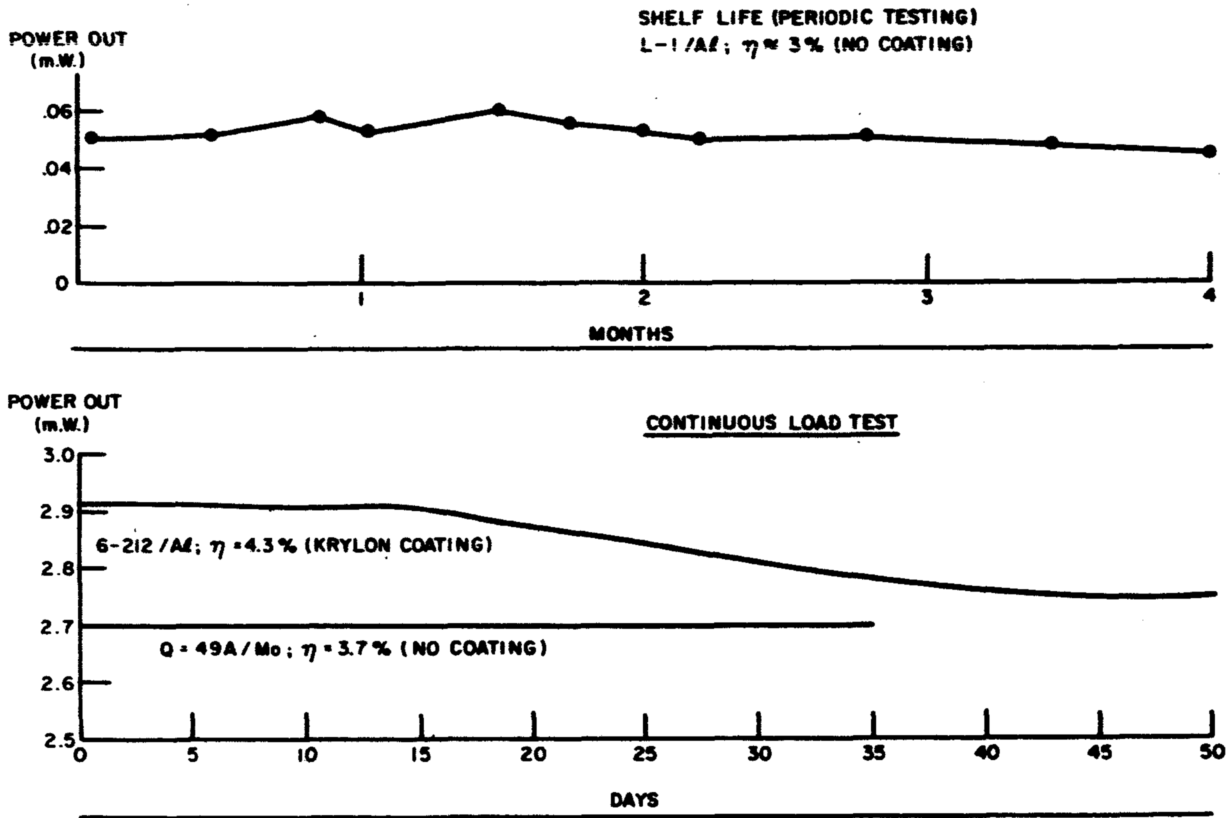


Fig. 13 Room ambient life tests, $Cu_{1.8}Se/GaAs$ cells.

V. CONCLUSIONS

Films of gallium arsenide on aluminum, of total thickness of 1.5 mils, are suitable for use in thin-film solar cells. Such films having reproducible electrical properties can be grown with a high yield by oxide transport from GaAs.

GaAs films can be grown from elemental Ga and arsine by halide transport or from the elements Ga and As by oxide transport of the Ga. Their suitability for cell production is not yet established.

Some cuprous selenide films on glass have remained stable in air for four months (others have shown a color change). The reasons for their stability are not known.

A $Cu_{1.8}Se$/GaAs/InAs/Al foil cell has shown an efficiency of 4.3% and a power-to-weight ratio of 135 W/lb.

Cells made with cuprous selenide-GaAs barriers on Mo substrates have been stable under continuous load for at least 40 days with no protection. The degradation rate of such cells on Al substrates has been greatly reduced by an etching treatment.

VI. RECOMMENDED AREAS FOR FUTURE WORK

Attempts should be made to grow larger area GaAs films from elemental Ga and As or AsH_3 using oxide transport of the Ga to see if this method has any advantages over halide transport.

Electron diffraction studies should be made of $Cu_{1.8}Se$ films in the "orange-brown" and "blue-grey" forms to determine the phases present. The conditions for producing a stable cubic phase should be found. The properties of even less stoichiometric cupric selenide films, e.g., $Cu_{1.6}Se$ should be determined.

When a stable cubic film of cuprous selenide can be made dependably, further studies of cell stability should be undertaken.

The effect of anti-reflection coatings on the spectral response of $Cu_{1.8}$/GaAs film cells should be studied with particular reference to trying to improve the response in the 1.5 to 2.0 eV range.

The performance of other barrier forming materials, e.g., CdO, $Cu_{1.8}Te$, should be determined.

VII. ACKNOWLEDGEMENTS

We wish to acknowledge the active cooperation of R. R. Addiss, Jr. during the earlier part of this year, and also the technical help of G. Mark and R. W. Pratt. The Materials Analysis Group headed by S. J. Adler has provided help with x-ray, electron diffraction, and chemical analysis studies.

APPENDIX

It is known that the accommodation coefficient α_1 of selenium on bare glass is low. The possibility is therefore raised that in the early stages of the flash evaporation of $Cu_{2-x}Se$, before the substrate is completely covered, Se which reaches the bare glass re-evaporates, leading to a different film composition $Cu_{2-y}Se$.

We make a "worst case" calculation under the following assumptions:

for Se on glass $\alpha_1 = 0$

for Se on Cu or $Cu_{2-y}Se$, $\alpha_1 = 1$

for Cu on glass $\alpha_3 = 1$

for Cu on $Cu_{2-y}Se$ $\alpha_4 = 1$

and further that the fractional coverage of the substrate C is related to the mass m' of film on the substrate by

$$C = km' \tag{6}$$

Suppose m grams of $Cu_{2-x}Se$ contains:

n atoms of Se of weight b (each)

and (2-x) atoms of Cu of weight a (each)

If dm grams of $Cu_{2-x}Se$ is incident on the substrate when the coverage is C, then

(2-x) a dn grams of Cu stick

and

Cbdn grams of Se stick

or

$$dm' = [(2-x)a + Cb]dn$$

Substituting for C from Eq. (6) and integrating

$$e^{kbn} = \frac{p + km'}{p} \tag{7}$$

where

$$p = (2-x)a/b \tag{8}$$

We define n_o as the value of n for which C = 1

$$e^{kbn_o} = \frac{p + 1}{p} \tag{9}$$

When dn atoms of Se are evaporated there is lost from the deposit (1 - C)dn atoms. The total loss $L = \int_0^{n_o} (1 - C)dn$. With the appropriate substitutions, this leads to

$$L = n_o \left[(1 + p) - \frac{1}{\log_e \frac{p+1}{p}} \right] \qquad (10)$$

For x = 0.2

$$L = n_o \ (0.56) \qquad (11)$$

giving a film composition $Cu_{4.09}Se$ at just complete coverage. With the further evaporation of $Cu_{2-x}Se$, y drops and approaches x.

Suppose that the completed film requires that $An_o(Cu_{2-x}Se)$ atoms be directed at the substrate then (for x = 0.2) y varies as:

A	y
1	4.09
2	2.95
3	2.37
10.5	2.0

We believe that in practice $A < 10$ and that $y \approx 0.2$. This implies that Se atoms reaching the glass migrate to $Cu_{1-x}Se$ islands and condense there before they can re-evaporate. A similar calculation by H. D. Lanyon of these Laboratories indicates that α_1 under these conditions must lie between 0.9 and 1.0.

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