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FABRICATION AND EVALUATION Final Report
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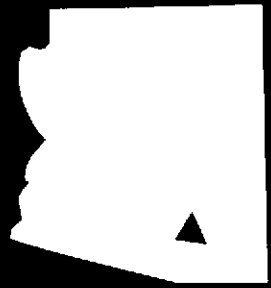
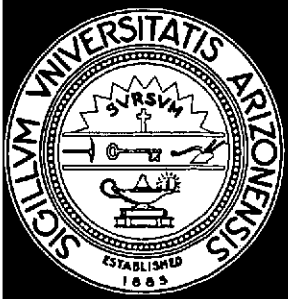
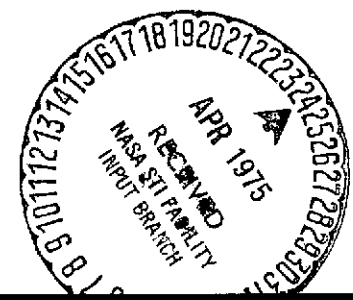
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FINAL REPORT

INVERSION LAYER SOLAR CELL FABRICATION
AND EVALUATION

JPL CONTRACT No. 953785

DECEMBER 1974



ENGINEERING EXPERIMENT STATION
COLLEGE OF ENGINEERING
THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

INVERSION LAYER SOLAR CELL FABRICATION AND EVALUATION

Final Report

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ABSTRACT

Inversion layer solar cells have been fabricated by etching through the diffused layer on p-type silicon wafers in a comb-like contact pattern. The charge separation comes from an induced p-n junction at the surface. This inverted surface is caused by a layer of transparent material applied to the surface that either contains free positive ions or that creates donor states at the interface. Cells have increased from 3 ma I_{sc} to 100 ma by application of sodium silicate. The action is unstable, however, and decays with time.

Other substances have been applied to achieve a stable inversion layer, but none were found. Encapsulation slowed the rate of decrease in the output, but did not stop it. Stable strong inversions are possible with tin oxide on n wafer mesa cells, but the contacts deteriorated slowly.

Non-mesa contaminated oxide cells were fabricated with short circuit currents of over 100 ma measured in the sun. Cells of this type have been stable for over a year.

SUMMARY

Transparent electrode cells that require a thin insulating coating of large area, with no leakage or shorts under bias, were extremely difficult to fabricate. Experiments designed to produce this layer were unsuccessful, yielding shorts or high leakage paths under bias. Substances such as silicon dioxide, silicon monoxide and sodium silicate were applied in various ways, and none yielded a defect-free transparent insulating layer.

The work on the transparent electrode cell was terminated and efforts directed to the development of a contaminated layer cell. The process developed seems to promise a cell which could be manufactured using state-of-the-art technology, and be adaptable to low cost large volume fabrication practices. An n-layer is first diffused on the silicon wafer surface; following diffusion of the n-layer, titanium-silver is then evaporated over the entire diffused surface. Using photolithography, a comb-like pattern is delineated exposing the titanium-silver. The titanium-silver is removed in the exposed areas by etching. With the photoresist still in place, the exposed diffused surface is then etched away exposing the base silicon. Mesas are thus formed. A coating of material designed to create donor surface states or supply positive ions on the surface is applied. Various substances were tried but the most successful was sodium silicate. A 2x2 mesa cell without an inversion region yields about 3 ma. After proper treatment with sodium silicate, outputs as high as 115 ma I_{SC} have been measured.

Other means of creating an inversion region such as sodium ions in silicon dioxide were not adequate.

Thus far, the sodium silicate layer has not produced a stable cell. After the sodium silicate is applied, the output decreases over a period of time to that of the cell before the sodium silicate was applied.

Other substances such as tin chloride and sodium borate were applied to the surface. These two did create a significant inversion layer, but many others did not. None produced a stable output.

The cells were potted in transparent substances and placed in evacuated chambers in an attempt to halt the degradation, but the decrease still occurred although at a slower rate.

Tin oxide on n wafers produced a p type inversion on mesa cells. Short circuit currents of 105 ma were obtained. These cells were also unstable; however, the instability is probably due to a deterioration of the contact rather than a loss of the inversion layer.

Stable contaminated oxide cells were fabricated but these are not of the mesa type. Short circuit currents of over 100 ma were achieved at 140 mw/cm^2 exposed to the sun.

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I. INTRODUCTION

A. Basic Conventional Cell Description

In a conventional diffused p-n junction, solar cell power is extracted from the cell by the separation of light generated hole electron pairs within the built-in electric field across the junction. This field results from the diffusion of p-type carriers (holes) from the p-type bulk into the n-type area and the diffusion of n-type carriers (electrons) into the p-type bulk.

The collection efficiency of a solar cell is the probability that a hole electron pair will be separated in the electric field before recombination takes place. The collection efficiency depends on how far away from the junction hole electron pair generation takes place and on the diffusion length of the generated carriers.

For maximum efficiency certain trade-offs must occur. A thick n region is desirable to obtain a low series resistance. However, a thick n layer means that hole electron pairs generated close to the surface by shorter wavelengths of light must travel a longer distance to reach the junction. This increases the probability that they will recombine before reaching the junction. The optimum junction depths must be selected from a compromise between these two criteria.

Another area where a trade-off occurs is in the doping level of the n diffusion. A high doping level is desired to obtain a low series resistance. However, a high doping level results in a short recombination time which will decrease the collection efficiency of the cell for shorter wavelengths of light.

The end result of these trade-offs is that efficiency in the short wavelengths of light is sacrificed in order to improve the overall performance of the cell.

B. Basic Transparent Electrode Cell Description

It is proposed that a solar cell with a thin induced inversion region would be more efficient in the shorter wavelengths of light than a standard diffused cell. This inversion region would occur right at the surface of the cell which would reduce the distance that hole electron pairs generated by short wavelengths of light would have to travel before being collected.

One method of inducing an inversion region is to use the capacitor principle to attract electrons to the surface from the bulk of a p-type wafer and to repel positive carriers away from the surface of a p-type wafer. This creates an inversion region next to the surface of the wafer. This principle is used in the transparent electrode cell whose cross section is shown in Fig. 1. The transparent electrode must be biased positively with respect to the back contact of the cell in order to induce an n region at the surface of the wafer. An electric field is formed across this inversion region similar to the electric field across the junction in a diffused solar cell. This electric field can be used to separate light generated hole electron pairs. The n diffusions shown in Fig. 1 are there to make contact with the inversion region.

An inversion region can also be induced in a p-type wafer by fixed positive ions in a transparent layer on the wafer surface.

The contaminated oxide cell uses sodium ions incorporated into a thermally grown silicon dioxide layer. The ions are introduced into the

silicon dioxide by mixing NaCl with the water that is boiled and passed through the furnace where oxidation takes place.

II. TRANSPARENT ELECTRODE CELL

A. Transparent Electrode Growth

The problems of growing a consistent transparent electrode have been solved by modifying the transparent electrode growth apparatus. The new setup is pictured in Fig. 2. It is believed that much of the SnO_2 was deposited on the sides of the long furnace tube in the old apparatus, rather than on the wafer. In the new apparatus the wafer is placed on a ceramic heating block and placed in a 10" long tube. The wafer is heated by passing a current through the tungsten wire incorporated in the heating block. The normal mixture of SnCl_3 fumes, nitrogen, and oxygen is then passed through the tube. This method produces more consistent results than the old method.

B. Low Temperature Insulating Oxides

In order to reduce the time and complexity involved in processing transparent electrode cells, much work was done in the area of growing low temperature oxides. Growth of oxides at relatively low temperatures increases cell efficiency in that a high temperature oxidation will cause lattice faults which reduce the recombination time for hole electron pairs. In addition, a low temperature oxide will not drive the n-diffusion deep into the wafer.

C. Methods of Testing Dielectrics

In order to test the dielectric integrity of the various oxides that were tried, a pattern of conducting dots was put on the oxide to be checked. A square array of eight dots on a side was used. Conducting silver

paint was used to form the dots. The breakdown characteristic of the oxide was then tested on a Type 575 curve tracer. Contact was made to the back surface of the cell by a brass block and a movable needle point was used to make contact to each dot in turn. Since the dots covered approximately 50% of the total cell area, a good estimate of the number of dielectric faults per unit area could be obtained. A diagram of this test apparatus is shown in Fig. 3.

In previous work with the transparent electrode subcells, it was found that a 3000 Å insulator was optimum. Using this oxide thickness, it was found that a positive bias with respect to the back contact of 50 v was sufficient to create a strong inversion layer. Therefore, all dielectrics fabricated were tested for breakdown at an applied voltage of up to 50 v.

D. Growth of SiO₂ Using SiCl₄

The first dielectric to be tried was SiO₂ grown at low temperature by a reaction of silicon tetrachloride and oxygen on the surface of the wafer. The apparatus used to grow the SiO₂ is shown in Fig. 4. Nitrogen is used as an inert medium to carry the SiCl₄ fumes into the reaction chamber where the SiCl₄ combines with the oxygen to form SiO₂.

Experiments were made using a wide range of temperatures and flow-rates in an effort to produce a faultless oxide layer. It was found that the flowrates of the nitrogen and oxygen had little affect on the oxide produced, or on the rate at which the oxide grew. Temperature was found to be the critical factor, and temperatures from 0°C to 300°C were tried. It was found that a temperature of 0°C produced the best SiO₂ layer using this method.

After applying the silver dots and testing, it was found that none of the areas tested would stand up to the 50v bias. The reason for this was evident after examining the oxide layer with a microscope. There were many pinholes and imperfections which would allow shorts to occur.

Next a commercially available spin-on oxide was tried. The spin-on oxide selected was Emulsitone's Silicafilm SiO_2 . The oxide was spun on at 5000 rpm which resulted in an oxide thickness of approximately 3000 Å. After spinning, the wafer was heated to 300°C for 5 minutes to harden the oxide layer.

Testing the oxide using the silver dot method showed that most of the cell area would not support a bias of 50v. Only about 10% of the area withstood the full 50v bias.

Again examination under a microscope showed that many pinholes and faults existed in the oxide layer. The pinholes were not as numerous or as large as those that occurred using the SiCl_4 and oxygen reaction method, however.

It was thought that spinning several thin layers whose thickness added up to 3000 Å would help alleviate the pinhole problem. If pinholes were a purely random occurrence, the probability of having a pinhole in an identical position through several layers of oxide would be small.

Again testing showed that only 10% of the cell area would withstand the 50v bias. Evidently once a pinhole is formed in the initial oxide layer, the defect will propagate through successive layers of oxide that are spun on at a later time. The exact cause of the pinhole problem is not clearly understood. It could be that there are extremely small particles in the spin-on oxide solution that cause pinholes. In addition, some sort of surface contamination could occur on the wafer even though the wafers were cleaned thoroughly before processing.

A spin-on SiO_2 made from methanol, deionized water, and silicon tetrachloride was tried. After the spin-on solution was mixed, it was thoroughly filtered in an effort to remove all particulate contamination. A single coat of SiO_2 was spun on at 5000 rpm and baked for 5 minutes at 300°C .

Again testing showed that only about 10% of the cell area would not break down under a 50v bias. Spinning several coats of the SiO_2 mixture on the wafer did not improve the 10% figure appreciably. The results obtained with the mixture of methanol, deionized water, and silicon tetrachloride produced the same results as had been obtained with the commercial spin-on.

E. Slow Evaporation of SiO

An evaporated coating of SiO was tested next. The SiO was evaporated at a slow rate in a vacuum of 10^{-5} Torr. It was thought that a slow evaporation rate might promote the formation of SiO_2 on the wafer surface through combination of the SiO and the residual oxygen in the vacuum chamber. It was

desired to form SiO_2 on the wafer rather than SiO due to the fact that SiO_2 has a higher dielectric breakdown.

Testing showed that approximately 60% of the cell area would not break down under a bias of 50v. Close inspection under a microscope did not reveal any pinholes. There could be small pinholes in the oxide that could not be resolved by the microscope, however. The evaporation of several thin coats of oxide to make up a 3000 Å dielectric did not improve the results. Again only about 60% of the cell area would take a 50v bias.

F. Sodium Silicate Insulating Layers

The dielectric that produced the best results was a spin-on solution of sodium silicate diluted with deionized water. A solution of two parts deionized water to one part sodium silicate was mixed and thoroughly filtered to remove any particulate matter. The sodium silicate was spun on the wafer at 500 rpm and baked for 5 minutes at 300°C.

It was found that 90% of the cell area would support a bias of 50v. Approximately half of the faults located were not shorted initially. These faults would appear at some period of time ranging from 5 minutes to 1 hour after the 50v bias was applied. It was also noted that some of the faults could be "burned out" by briefly applying a high voltage to the silver dot where the fault was located. Unfortunately, not all of the short-circuited areas could be repaired this way.

G. Discussion of Perfection of Insulating Layers

None of the low temperature dielectrics fabricated would be suitable for a full 2x2 cm transparent electrode solar cell. Many wafers were fabricated using the different dielectrics and not one was entirely free of dielectric breakdowns at a bias of 50v.

In order to obtain a comparison between the dielectric strength of the low temperature dielectrics and a high temperature steam grown oxide, the silver dot pattern was applied to a wafer with a 3000 Å steam grown oxide. Every silver dot in the 8x8 matrix withstood a 50v bias. The bias had to be increased to nearly 100v before breakdown occurred.

The fact that no breakdowns occurred was not consistent with results obtained in fabricating the transparent electrode subcells. It was found when testing the subcells that approximately 20% of the subcells on each wafer exhibited some form of breakdown before a bias of 50v was reached.

The 20% failure for the subcells can be explained by the fact the HF etch faults exist in thermally grown SiO_2 layers. The HF penetrates into and removes the SiO_2 in the faults very quickly. This leaves an opening where the transparent electrode material can short to the p-type surface of the wafer very easily. These electrical short circuits caused by etch faults make processing a full 2x2 cm transparent electrode cell even with a thermally grown oxide nearly impossible.

H. Spin-on Transparent Electrodes

A commercially available spin-on transparent electrode material was evaluated to find out whether or not it could be etched successfully without the use of HF. The material used was Emulsitone Solution #673. After the wafer had a 3000 Å thermal oxide grown on the surface, the spin-on transparent electrode was spun on and baked. A photoresist pattern was applied over the transparent electrode. A paste made of powdered zinc and Karo syrup was painted over the surface of the wafer and the wafer was placed in a solution of one part deionized water to one part HCl. This procedure removed most of the transparent electrode material from the areas to be etched. Successive

etches did not remove any more of the undesired transparent electrode. HF removed the remaining transparent electrode material, however, but the use of HF resulted in the occurrence of short circuits from the transparent electrode to the p-type silicon wafer.

At this point it was decided to abandon efforts to produce a large area transparent electrode cell. The problems associated with fabricating a perfect dielectric and etching of the SiO_2 layer cannot be solved with current processing techniques. Work was then started on the Mesa cell as described in the following section.

III. MESA CELL

A. General Description

The Mesa Cell as pictured in Fig. 5 was constructed by diffusing an n-type dopant into a 2x2 cm p-type wafer. Then the metal contact was evaporated over the front surface of the wafer. Photoresist was applied and developed into the contact pattern. The metal was then etched from the areas not protected by photoresist. A silicon etch was used to remove the n diffusion from all areas not covered by the metal contact pattern. Metal was evaporated over the back surface of the wafer and the wafer was sintered. A layer of transparent material having the property of inducing an inversion layer in the surface of the semiconductor was then applied to the front surface of the wafer.

The primary advantage of the Mesa Cell is the short amount of time required to process cells. Two high temperature oxidation steps and a low temperature diffusion were needed to fabricate contaminated oxide cells. A single low temperature diffusion is all that is required in the processing of a Mesa Cell. The lack of exposure to high temperatures

(1100°C or above) will tend to increase the efficiency of the Mesa Cell. Exposure of single crystal silicon to a thermal cycle from room temperature to 1100°C or more and then back to room temperature creates lattice faults which tend to reduce the recombination time which will lead to an overall decrease in efficiency of a solar cell.

Three photoresist steps are required in the processing of a contaminated oxide cell, one to open holes in the initial oxide to allow diffusion to occur, one to open contact areas in the contaminated oxide, and one to etch the metal contact pattern. Only one photoresist operation to etch the metal pattern is required to fabricate the Mesa Cell. The simplified process schedule also increases the yield for a given batch of cells.

The procedure of diffusing the entire surface of the Mesa Cell eliminates many of the leaky junctions that can occur in the processing of Contaminated Oxide Cells, due to high leakage from contact to the p wafer. During the first photoresist process in fabricating Contaminated Oxide Cells, either defects in the mask or impurities in the photoresist could cause spots of photoresist to remain over areas that should be etched off to allow diffusion to occur. This would result in electrical short circuits across the junction due to the metal contacts making electrical connection to the p-type bulk.

B. Mesa Cells with Aluminum Contacts

The first successful Mesa Cells had a junction depth of 3-4 μ which resulted from a 40 minute POCl_3 diffusion at 945°C. The silicon was etched to a depth of approximately 7 μ . A solution of 5 ml of HF to 45 ml of nitric acid was used to etch the silicon.

Aluminum was used as the contact metal because of its resistance to the silicon etchant. Even if the protective photoresist peels off the aluminum contact pattern during the silicon etch, the aluminum will not be entirely etched off during the remainder of the etch. A detailed process schedule for the Mesa Cell is given in the Appendix.

The sodium silicate, used as the contaminated spin-on source, was made from a solution of two parts deionized water to one part sodium silicate with 1% by weight of NaCl added. It was found that this sodium silicate layer formed a good antireflection coating. The spin-on sodium silicate layer is also transparent to short wavelength light.

The V-I curve for the first successful Mesa Cell is shown in Fig. 6. Immediately after the sodium-silicate spin-on and a 5 minute heat treatment at 250°F, the cell output was raised from 5 ma to 90 ma short circuit current; the open circuit voltage was 0.54 volts. The efficiency of this cell is 3.2%. The low efficiency and poor curve factor of this cell is due to several reasons, among them are the following: Aluminum is not the optimum contact material due to a significant series resistance between the aluminum and the silicon. The induced inversion is very thin which will also produce a high series resistance. And, a contact pattern with thirty or forty fingers rather than the twenty finger pattern used on this cell, should decrease the series resistance caused by the thin inversion region.

It was noted that over a period of several days the output of the cell dropped from 90 ma to 75 ma. The lower value of short circuit current indicates that the inversion region had diminished. A five minute heat treatment at 250°F brought the short circuit back up to 90 ma. It is thought that

the degradation in output over a period of time could be due to the humidity in the atmosphere penetrating the sodium silicate layer and through some mechanism passivating the contaminated layer.

C. Mesa Cell with Titanium-Silver Contacts

The next group of Mesa Cells that were processed had titanium-silver contacts. Titanium-silver contacts were used in an effort to reduce the series resistance of the cell. Much difficulty was encountered in doing the silicon etch after the titanium-silver contact pattern had been etched. The silicon etchant would undercut the titanium-silver very quickly causing the photoresist to lift around the periphery of the contact pattern resulting in severe contact damage.

The output of cells constructed using a shorter silicon etch time would not increase appreciably after spinning on sodium silicate, and heat treating. This was thought to be caused by the stained area around the periphery of the contact pattern where the silicon etch had attacked the titanium-silver. This stained area could be insulating the inversion layer from the n diffusion.

D. Wax Etch Masks

In order to overcome the problem of undercutting that occurred when photoresist was used as a mask against the silicon etch, a method of using Apiezon wax as a mask against the silicon etch was devised. A set of twenty

razor blades with spacers between the blades was used as a stencil to apply the wax. The wafer to be etched was heated to a temperature slightly greater than that required to melt the wax. The razor blades were dipped in molten wax and pressed down on top of the wafer. This left a set of twenty parallel lines of wax on the wafer. The broad center contact was put on with a thicker blade using the same method. The wax pattern solved the undercutting problem and it was possible to do a deep etch (7μ) without seriously undercutting the titanium-silver contact.

Again, after spinning on sodium silicate and giving the wafers a five minute heat treatment, the outputs did not come up appreciably. The outputs ranged from 5 ma to 7 ma. Close inspection of the wafers under the microscope again revealed a stained area around the periphery of the contact area. As before, this was thought to be the reason for the poor output obtained.

The titanium-silver contacts did improve the series resistance of the cell. A resistance of $.5 \Omega$ was obtained with titanium-silver versus the $.8 \Omega$ series resistance obtained when aluminum contacts were used.

E. Buffered Silicon Etch

At this point a number of experiments were performed to develop a milder silicon etch that would be compatible with the photoresist process and that would not cause staining. It was found that a silicon etch consisting of, by weight, 8% hydrofluoric acid, 32% nitric acid, and 60% acetic acid met the preceding criteria. In order to prevent staining from occurring, the beaker containing the silicon etchant and the wafer undergoing the etching process had to be quenched with large amounts of deionized water when the etch was terminated.

A group of cells was fabricated using the new silicon etch solution. Prior to spinning on sodium silicate, the cells were examined under a microscope. There was no appreciable staining evident around the contact fingers. Again, after spinning sodium silicate and heat treating the wafers for 5 minutes at 250°F, the outputs remained low.

F. Low to High Output

After a period of approximately two weeks, all Mesa Cells previously fabricated were retested using a different heat treatment. The heat treatment started out at 250°F and progressed to 700°F in 50°F increments.

A V-I curve for a typical Mesa Cell with aluminum contacts is shown in Fig. 7. The short circuit current is 92 ma and the open circuit voltage is .46v after a heat treatment of 5 minutes at 250°F. After a heat treatment of 5 minutes at 400°F, the short circuit remains at 92 and the open circuit voltage increased to .5v. After a further heat treatment of 5 minutes at 600°F, the short circuit current increased to 96 ma and the open circuit voltage increased to .52 volts. The efficiency of this cell increased from 2.9% to 4.4% after heat treatment. The V-I curves for this cell after the 400°F heat treatment and the 600°F heat treatment are shown in Fig. 8 and Fig. 9.

A V-I curve for a Mesa Cell using titanium-silver contacts with the razor blade pattern is shown in Fig. 10. The short circuit current is 100 ma and the open circuit voltage is .52v. An efficiency of 4.9% is obtained with this cell. Initially, the output on this cell was low. After a period of several weeks, the cell was given a further heat treatment to 700°F which produced the results given.

A V-I curve for a Mesa Cell with titanium-silver contacts that was etched using the photoresist process is shown in Fig. 11. The short circuit current is 110 ma and the open circuit voltage is .49 v. This cell was given a heat treatment up to 700°F which produced the results given. The overall efficiency of this cell is 4.3%.

G. Degradation of Cell Output

All cells whether constructed with aluminum or titanium silver contacts will degrade over a period of time. The rate of degradation will vary widely from cell to cell. Some degrade significantly in a matter of hours and some require several days. All of them will eventually degrade to the same value obtained before the inverting material was applied.

This degradation is thought to be due to the formation of a passivating oxide layer on the silicon surface. A slight room temperature oxide exists on the surface before the sodium silicate is spun on, and the heat cycle causes the sodium silicate to penetrate this slight layer and act with the surface to cause surface states. At this point the output of the cell will be comparatively high. The surface will, in time, oxidize again, thereby passivating the surface and reducing the surface state density. Eventually the state will be eliminated and the cell output return to the original output. Further heating will start the cycle again with high output and subsequent degradation.

H. Encapsulation

Evidence exists that the degradation of the cell is enhanced by the intervention of water vapor on the surface. Sodium silicate is deliquescent and the output decrease can be very rapid if it is dipped in

water or "breathed on". Encapsulation to prevent water vapor from reaching the surface may be an answer to the problem.

Several inversion Mesa Cells were maintained for a number of days in a dessicator that was evacuated with a vacuum pump. Frequent I_{sc} measurements were made to follow the decreasing output of the cells. The cells were then left out of the desiccator and the output measured periodically. Figure 12 shows the results for one such cell, and Fig. 13 for another. Both cells show a definite dependence on an isolated atmosphere to keep from deteriorating rapidly.

Humidity is probably not the direct cause of cell output decrease but acts like a catalyst to enhance another cause of deterioration such as an oxide layer. A strong indication that the latter is true is the decrease in the cell output while in the desiccator. The output should decrease only to the extent that it was exposed to the atmosphere during measurement. Water vapor is retained by the sodium silicate, however, and even though the atmosphere surrounding it in the desiccator has no water vapor, the water vapor that was absorbed might not leave the sodium silicate layer and continue to degrade the cell. Heating usually restores the high output of the cell by driving the water vapor out and restoring the mechanism creating the inversion layer in the first place.

Attempts at encapsulation were unsuccessful. The output of a cell was followed for a few days and its rate of change observed. The cell was brought up to maximum performance again and a coating of Krylon sprayed on the surface. The output still decreased but at a slower rate. Another cell was chosen whose I_{sc} output was 8 ma. After heating the output rose to 38 ma. A thin sheet (.001") of mylar was cemented on the cell with Krylon and

the output of the cell dropped to 32 ma. After two hours the cell dropped to 6 ma. This type of encapsulation obviously does not work.

A cast type epoxy resin was used to encapsulate the cell, but after the encapsulation, contact to the cell was rather difficult. Any attempt to remove the encapsulant also removed the metal contacts. Leads could not be soldered to the cell before encapsulation because the cell has to be heated to temperatures quite above the soldering temperature. Trying to solder after sodium silicate is applied is also a problem. Our attempts at encapsulation were not successful.

I. Inverting Material Evaluation

The search for a transparent material that has the property of creating a stable inversion layer in silicon was initiated and a number of different chemicals were evaluated. A total of fourteen compounds were tested, mostly from the Group IV and V elements. Two methods of application were employed where circumstances permitted: spin-ons using a high speed photoresist spinner, and melting compounds directly on the cells.

In general, the cells were subjected to a heat cycle after having the contaminant applied. Their behavior after spin-on, during heating, and through the subsequent observation period, has been noted and tabulated in the data section of this report.

Four series of cells are found in the discussion of experimental results. Series "A" and "E" are titanium-silver contact cells using a 20 minute predeposition in POCl_3 at 945°C . The "A" cells were etched for fifteen seconds in 45-16-4 etch (HAC, HNO_3 , and HF in milliliters, respectively). The series "E" cells were etched for forty seconds in 60-16-4 etch.

The "B" and "C" series cells are aluminum contact cells using the same predeposition. Both series were etched forty seconds in 60-16-4 etch. Group IV and V element compounds were evaluated because it was felt that their characteristics would aid in the formation of surface states on the cell.

Many of the theoretically promising chemicals could not be tested for a variety of reasons. Several were of the exotic variety, unavailable commercially. Others, most notably arsenic and phosphorous compounds, were deleted due to the difficulty and danger of handling the materials. The chemicals tested were compounds of antimony, bismuth, lead, selenium, tin, and several phosphate compounds. The phosphates were used to represent the phosphorus group as the phosphorous compounds which were available were highly toxic and volatile. In general, the chemicals were selected on the basis of transparency, solubility, melting point, and general availability.

Data in Chronological Form

The fourteen contaminant solutions were applied and tested in numerous ways. The most noteworthy results for each contaminant will be stated, with subsequent reference to further information contained in the data tabulation section. The reference notes refer to individual cell designations in Table 1.

Antimony Trichloride

Antimony trichloride was spun on two silver-titanium cells and caused a post spin increase for 73 to 87 ma and from 11 to 13 ma on the two cells. Heating the higher output cell through a standard heat treatment caused the output to decrease and stabilize at 80 ma. The compound changed

to an opaque white coating at approximately 600°F. The net increase of 7 ma was stable over a two-week period. Application by melting the antimony trichloride resulted in a slightly translucent even coating with the cell output dropping from 19 to 14 ma.

Sodium silicate was spun on in conjunction with antimony trichloride to determine the extent of interaction, if any. The cell dropped from an initial value of 7.5 ma to 4 ma. Heating increased the output to 6.2 ma, but the cell deteriorated to 4 ma with time. (Cells A2, A3, C4)

Bismuth Nitrate

This contaminant was spun on in a standard solution of one gram per ten milliliters of acetone. The output increased from 3.3 to 8.7 ma, but decreased during heating and stabilized at 3.8 ma. The net increase of 0.6 ma was stable for two weeks. This gain may be due in part to calibration error on the probe station. (Cell A10)

Bismuth nitrate was melted on an aluminum contact cell to compare its effect with that of the spin-on method. An opaque white coating resulted, decreasing the output from 22 to 18.5 ma. The compound also reacted with the metallization with time to reduce the output to zero. (Cell C1)

Bismuth Trichloride

The compound was spun on an aluminum contact cell and increased the output from 8.2 to 8.6 ma. Heating produced no appreciable increase. The cell shorted within 96 hours due to the reaction of the contaminant with the contacts. (Cell B7) Bismuth trichloride when melted on an aluminum cell resulted in a loss of output from 18 to 1.4 ma. (Cell C3)

Lead Acetate

Lead acetate was spun on in standard solution (1 gm in 10 ml DI water) on a titanium-silver cell. The output increased from 4.2 to 5.2 ma, and reached a peak of 5.8 at 500°F during the heat cycle. The output decreased to 4.8 ma within 7 days. (Cell A4)

Melting the lead acetate onto an aluminum cell resulted in a translucent coating which decreased the output from 74 to 68 ma, at which point it stabilized. (Cell C5)

Lead Chloride

This contaminant was spun in standard solution onto a Ti-Ag cell and caused an immediate decrease from 3.4 to 2.9 ma. Heating reduced the output further to a minimum of 1.6 ma at 700°F. Upon cooling, the cell stabilized at 2.6 ma and remained there for 14 days. (Cell A 11)

Lead chloride was not applied by melting due to its high melting point. (501°C)

Selenium Dioxide

The compound was spun on two Ti-Ag cells in standard solution. The outputs increased from 60 to 63 and from 19 to 23 ma. Heating had no discernable effect on the outputs, and the compound gave off strong noxious vapors during the heat cycle. Both cells were stable for at least several weeks. (Cells A1, A5)

Sodium silicate was spun on one of the cells and given a heat treatment. The output increased from 20 to 24 ma and peaked at 100 ma at 700°F. The cell decreased to 22 ma within 48 hours. Reheating did not regain the high output. (Cell A5)

Sodium Stannate

The contaminant was spun on an aluminum contact cell with a resultant increase from 25 to 28 ma. A peak output of 40 ma was attained at 800°F during heat treatment. The cell decreased to its original value of 25 within 96 hours.

Melting sodium stannate crystals onto an aluminum cell failed to produce a coating due to its change to anhydrous sodium stannate at 140°C.

Stannous Chloride

Extensive experimentation was performed using various strengths of stannous chloride solutions after initial test yielded significant increases in output.

The contaminant displayed a characteristic behavior during testing. In general, it caused an increase of between ten and fifty percent after spinning. Heating caused fumes to be given off and a chemical change to an oxide of tin occurred at approximately 700°F. The output then stabilized for long periods of time at the value attained during the change to tin oxide.

The most notable results were the application of a 1.5 gm to 10 ml methanol solution which increased output from 70 to 106 ma upon heating. All cells having stannous chloride heated on their surfaces were very stable with time. (Cell A6, A8, A12, E1)

Three solutions of stannous chloride were then prepared, with 0.5, 1.5, and 2.5 grams per 10 ml methanol in the "DELTA", "ALPHA", and "BETA" solutions, respectively. The three solutions were applied to Ti-Ag cells and heat treated. The process was repeated three times, and the

characteristic behavior was evident as the compound increased the post-spin output and further peaked during heating. Using the weak solution (.5 gm/10 ml methanol) through three applications and heat treatments, the output increased from 3.3 to 14 and stabilized. (Cell E2)

The "ALPHA" solution (1.5 gm/ 10 ml methanol) which was of the same strength as the original test solution of stannous chloride, was applied and heat treated three times. The output increased from 3 to 23 ma but, in this isolated case, was unstable and decreased to 5.7 after 96 hours. This was the only instance where a stannous chloride cell was unstable, and may be due to imperfections of the cell itself. (Cell E3)

The strong saturated solution "BETA" was also applied and heated three times with significant results. After the first heat cycle, output rose from 4.4 to 16 ma. The second application increased output to 74 ma, but heating decreased it to a stable 21.5 ma. The third process yielded a stable cell with a 60 ma output. (Cell E4)

Two subsequent cells were treated three times with the strong solution but heated only twice. Their outputs rose from 3.7 to 23 and 5.0 to 33 ma. (Cells E6, E7)

The strong solution was then applied without heating on one cell and two coats with one heat cycle were applied to a second cell. The latter output increased from 4.8 to 32 ma and stabilized at 20 ma with time. (Cells E8, E9)

Two other experiments were performed using stannous chloride. Sodium silicate was spun on cell A6 and heated. The output increased from 13.5 to 55 but decreased to 4 ma within 96 hours. (Cell A6)

Stannous chloride was also melted onto a Ti-Ag cell, increasing output from 4.1 to 6.4 but the output decreased and stabilized at 4.2 with time. (Ref. E5)

Several aluminum contact cells were spun with differing strengths of stannous chloride with the characteristic results. However, the compound attacks aluminum and, hence, the cell outputs deteriorated rapidly with time. (Cells B9, 10, 11, 12)

Mercuric Nitrate

Mercuric nitrate was experimented with due to its availability, as it is a Group II element rather than a IV or V. Spinning it on an aluminum contact cell dropped the output from 46 to 30 ma. However, the output increased over a 96 hour period to 54 ma and stabilized at that point. No heat treatment was applied so the increase apparently took place as the cell dried. (Cell B8)

Melting on mercuric nitrate increased output from 35 to 36 ma, but dropped to 12 ma over a 6-day period. (Ref. C2)

Ammonium Phosphate

Spinning on this contaminant decreased the output of an aluminum cell from 14 to 12.5 ma. Heating produced a peak of 18 at 500°F, but the output decreased to its original value of 14 within 7 days. (Cell B1)

Melting ammonium phosphate on an aluminum cell decreased the output from 68 to 10 ma. An even coating was unattainable and some reaction which disrupted the back contact was observed. (Cell C6)

Calcium Phosphate

Two standard 1 gm to 10 ml solutions were made, one of DI water and one of methanol. The alcohol solution spun on an aluminum cell produced an increase from 17 to 21 ma, stable with time after heating. (Cell B2) The water solution did not yield as even a coating and showed no significant change in output. (Cell B3)

An attempt at melting the calcium phosphate onto an aluminum cell was unsuccessful as its melting point is too high for the available equipment. (Cell C7)

Potassium Phosphate

The compound was spun on an aluminum contact cell with a resultant increase from 41 to 52 ma. Heating caused a peak output of 54 ma at 700°F, but the cell was unstable and decreased to 44 ma over a two week span. (Cell B4)

Melting potassium phosphate yielded a smooth transparent surface but dropped the output from 25 to 8.6 ma. The coating remained liquid rather than recrystallizing. (Cell C8)

Sodium Metaphosphate

A standard solution was spun on an aluminum contact cell and yielded an increase from 35 to 43 ma. Heating gave a peak of 48 ma at 400°F, but the output was unstable and decreased to 36 within one week. (Cell B5)

Sodium metaphosphate was melted on an aluminum contact cell and increased the output from 70 to 76 ma. The increase was stable with time. (Cell C10)

Trisodium Phosphate

A standard solution in water spun on a Ti-Ag cell decreased the output from 5 to 2.8 ma. Heating showed a peak of 12 ma at 700°F. The output was unstable, however, and decreased to 4.6 ma within 24 hours. (Ref. A7) Sodium silicate was spun on in conjunction with the trisodium phosphate and increased the output from 3.4 to a maximum of 40 ma at 600°F. The cell decreased to 4 ma within 24 hours. (Cell C11)

Conclusions

A brief paragraph will be devoted to each of the contaminants which were tested, covering the conclusions drawn from the experimental results previously described.

Antimony trichloride caused an increase in output after spin on, but heating decreased the net gain. An opaque coating was formed that gave a stable 10% increase. This gain is attributed to the antireflective properties of the coating. Sodium silicate in conjunction with the antimony trichloride did not appreciably affect the output. The nature of the gain in output shows antireflection but no significant surface state activity.

Bismuth nitrate increased the output several times but the cell was unstable when heated. The small net gain of about 15% is due to antireflection. Melting the compound created an opaque white surface. The contaminant is unsuitable for use on aluminum contact cells as it reacts slowly with the metal.

Bismuth trichloride also reacted with aluminum contact over a 96 hour period. A negligible increase was noted prior to heating, due to a small antireflective property. No surface state presence was discerned from the cell's behavior.

Lead acetate caused an increase of 24% before heating but the output decreased to a net gain of .6 ma (14%). The magnitude of this change indicates antireflection rather than creation of an inversion layer as being responsible. The contaminant formed a smooth translucent layer upon melting but did not increase the output.

Lead chloride was responsible for an immediate and stable decrease in output. No antireflection increase nor other activity was noted. Melting was not attempted due to the high melting point of the compound.

Selenium dioxide gave a stable but small increase of between 5 and 15%. The compound left a clear, relatively uniform coating which increased the output by its antireflective qualities. Sodium silicate in conjunction with the selenium dioxide created a significant increase of 80 ma (400%) but was highly unstable. The two compounds in company might be useful if a method of encapsulation is developed which would stabilize the output. However, most of the increase should be attributed to sodium silicate as the cell followed that compound's characteristically dramatic increase and subsequent instability.

Sodium stannate yielded a 20% increase upon application but subsequent heating did not prevent the cell from deteriorating to its original value within 96 hours. The unstable gain can be attributed mostly to antireflective coating action. The compound appears to lose its effectiveness upon continued contact with the atmosphere.

Stannous chloride was by far the most exhaustively tested contaminant, based on early successful results. The gain in output stabilized at the time when stannous chloride underwent a change to a tin oxide. The coating was transparent and displayed diffraction colors. Its application

yielded a stable increase of an average of 40%. This indicates the presence of an inversion layer of some intensity plus the action of a good antireflective coating. The ultraviolet response averaged less than 1.0 ma so the presence of an inversion layer is not responsible for the major portion of the increase. Therefore, stannous chloride is an excellent antireflective coating relative to the other compounds tested.

Melting stannous chloride left a clear smooth layer but difficulty was encountered in attaining good contact on the probe station. It did not cause a significant change in output since the compound remained in a chloride rather than oxide form. Stannous chloride with sodium silicate showed the characteristic silicate behavior with no noticeable effect due to the tin compound's presence. The chemical attacks aluminum contacts and, hence, is not suitable for use on aluminum cells.

Mercuric nitrate yielded a 15% increase after its solution had dried on the cell surface. The increase was stable with time and apparently was due to antireflection. The ultraviolet response changed antireflection. The ultraviolet response changed negligibly so an inversion region was not responsible for the increase.

Ammonium phosphate had no net effect on cell output when spun on. Melting did not yield a continuous coating and decreased the output significantly.

The calcium phosphate in alcohol gave a stable 20% increase due to antireflection. In water solution an even coating was unattainable and showed no effect on the output.

Potassium phosphate caused a 25% increase upon spin-on, but the net effect over a 14 day period was negligible. Melting yielded a smooth coating which would not harden and drastically reduced output.

Sodium metaphosphate showed a momentary 25% increase but the output deteriorated to its original value within 7 days. Melting caused a stable 10% increase.

Trisodium phosphate was applied by spinning, melting, and with sodium silicate. In all three cases it responded with unstable initial increases and regained its original value within 24 hours.

The phosphate group described above generally responded in the same manner. Ammonium phosphate showed no net effect, as did calcium phosphate in water, potassium phosphate, sodium metaphosphate, and trisodium phosphate. Those gains which did occur were of magnitudes which suggest antireflective action. The exception to this is trisodium phosphate in conjunction with sodium silicate, where the characteristic large increase occurred when the compounds were heated. The effect in this case is attributed to sodium silicate rather than the phosphate.

Taken as a group, the contaminants tested did not yield a compound which created a strong inversion region that was stable over long periods of time. In general the increases in overall cell output were not accompanied by additional ultraviolet response. The most significant result of this project is the performance of stannous chloride as an excellent antireflective coating. This compound yielded by far the most stable and predictable data among the experimental results.

Table 1. Results of Test on Contaminant Solutions

Contaminant	Cell	Initial	Post	High	Remarks
SeO_2	A1	60.	62.	62.	Heat causes decrease.
SbCl_3	A2	73.	87.	87.	Heat causes decr. Stable at 80
SbCl_3	A3	11.	13.	15.	Peak at 700 deg.F.
$\text{SbCl}_3 + \text{Na}_2\text{Si}_4\text{O}_9$	A3	7.5	4.	6.2	" " " " Unstable.
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	A4	4.3	5.2	5.8	" " 500 " Unstable.
SeO_2	A5	19.	20.	23.	No increase by heating. Stable.
$\text{SeO}_2 + \text{Na}_2\text{Si}_4\text{O}_9$	A5	20.	24.	100.	Peak at 700 deg.F. Unstable.
$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	A6	11.	8.	14.	" " " " Stable.
$\text{SnCl}_2 + \text{Na}_2\text{Si}_4\text{O}_9$	A6	13.5	3.5	55.	" " " " Unstable.
Na_3PO_4	A7	5.	2.8	12.	" " " " Unstable.
$\text{Na}_3\text{PO}_4 + \text{Na}_2\text{Si}_4\text{O}_9$	A7	3.4	3.5	40.	" " 600 " Unstable.
SnCl_2	A8	79.	86.	106.	Peak at 500 deg.F. Stable.
None	A9	98.	-	100.	Stained during processing.
$\text{A9} + \text{Na}_2\text{Si}_4\text{O}_9$	A9	100.	100.	100.	1st coat. Decreased with heat.
$\text{A9} + \text{Na}_2\text{Si}_4\text{O}_9$	A9	86.	115.	125.	2nd coat. 700 deg. peak. Unstable.
$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	A10	3.3	8.7	8.7	Decreased when heated.
PbCl_2	A11	3.4	2.9	3.4	Decreased when heated.
SnCl_2	A12	4.5	12.	12.	3 coats. Fast heat. Unstable.
$(\text{NH}_4)_2\text{HPO}_4$	B1	14.	12.5	18.	Decreased to initial value.
$\text{Ca}_3(\text{PO}_4)_2$	B2	17.	18.	21.	Methanol solution. Stable.
$\text{Ca}_3(\text{PO}_4)_2$	B3	40.	38.	40.	Water solution. Unstable.
K_2HPO_3	B4	41.	52.	54.	Peak at 700 deg.F. Unstable.
Na_2HPO_4	B5	35.	43.	48.	Peak at 400 deg.F. Unstable.
$\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	B6	25.	28.	40.	Decreased to initial value.

Table 1 (Continued)

Contaminant	Cell	Initial	Post	High	Remarks
BiCl_3	B7	8.2	8.6	8.6	Cell shorted in 96 hours.
$\text{Hg}(\text{NO}_3)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$	B8	46.	30.	54.	No heat. Incr. over time.
SnCl_2 (β)	B9	21.	32.	32.	Heat causes decrease.
SnCl_2 (δ)	B10	13.	20.5	20.5	Heat causes decrease to 16.
SnCl_2 (γ)	B11	42.	54.	54.	Heat causes decrease to 40.
SnCl_2	B12	29.	15.	15.	Deteriorates Al with heating.
$\text{Bi}(\text{NO}_3)_3$	C1	22.	18.5	18.5	Decr. to zero. Melted on.
$\text{Hg}(\text{NO}_3)_2$	C2	35.	36.	-	Decr. to 15. Melted on.
BiCl_3	C3	18.	1.4	-	Stable at 12 with time.
SbCl_3	C4	19.	14.	-	Decr. to 0. Melted on.
$\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$	C5	74.	68.	-	Stable at 74. " "
$(\text{NH}_4)_2\text{HPO}_4$	C6	68.	10.	-	Will not form coating.
$\text{Ca}_3(\text{PO}_4)_2$	C7	82.	82.	-	Will not melt on hotplate.
K_2HPO_3	C8	25.	8.6	-	Will not form solid coating.
Na_2HPO_4	C10	70.	76.	-	Stable at 76 over time.
Na_3PO_4	C11	30.	42.	-	Decr. to 36 within 24 hrs.
SnCl_2 (δ)	E1	4.4	5.6	12.	Peak at 800 deg. F. Stable.
" (δ)	E1	12.	22.	25.	2nd coat. 700 deg. peak. "
" (δ)	E2	3.3	3.4	10.	1st coat. Stable at 5.4.
" (δ)	E2	5.4	11.	8.4	2nd " " " 7.4.
" (δ)	E2	7.4	11.5	14.	3rd " " " 14.
" (α)	E3	3.	3.	9.2	1st " . Stable at 4.
" (α)	E3	4.	12.	18.	2nd " . " " 4.2.
" (α)	E3	4.2	23.	23.	3rd " . Decr. to 5.7 (96 hr)

Table 1 (Continued)

Contaminant		Cell	Initial	Post	High	Remarks
SnCl ₂	(β)	E4	4.4	5.2	16.	1st coat. Stable at 16 after ht.
"	(β)	E4	16.	74.	74.	2nd " . " " 21.5 " " .
"	(β)	E4	21.5	52.	60.	3rd " . " " 60. " " .
SnCl ₂	(crystals)	E5	4.1	4.	6.4	Stable at 4.2 after melting.
"	(β)	E6	3.7	3.	15.	1st coat. Stable at 15 after ht.
"	(β)	E6	15.	28.	28.	2nd " . " " 25 " " .
"	(β)	E6	25.	26.	26.	3rd " . " " 23. No 3rd heat.
"	(β)	E7	5.	3.7	20.	1st coat. Stable at 20 after ht.
"	(β)	E7	20.	38.	38.	2nd " . " " 20.5 " " .
"	(β)	E7	20.5	25.	31.	3rd " . " " 31. No "3rd" .
"	(β)	E8	2.2	2.6	3.2	No heat. 1 coat. Stable at 2.8.
"	(γ)	E9	4.8	2.4	8.2	1st coat. Peak at 800 deg. F.
"	(γ)	E9	8.2	32.	32.	2nd " . Stable at 20.

J. Tin Chloride Spin On

Because tin chloride applied to a cell and heated caused a change that resulted in a medium output comparatively stable cell, further work was done on this material. Several groups of cells were fabricated. Significant increases were noted for runs K and L.

These cells were allowed to set for a day before applying SnCl_2 and after the heat cycle the outputs increased. For instance, K4 increased from an initial 3.5 ma to 29 ma after spin and heat, and further to 62 ma 2-1/2 hours later with no further attention. After 70 hours, K4 increased to 72 ma I_{sc} , and remained around this value for several weeks and then started to slowly decay. Cell No. K8 remained about 50 ma for more than a month.

Series L also had several cells that remained stable for at least a month, but the output of these cells was lower than series M, between 30 and 40 ma I_{sc} . A visible change took place on the surface of the cell to the degree that the surface looked roughened and diffused, and not clear and reflective. The SnCl_2 must attack the surface and cause surface states by a slight agitation of the surface. If so, the recombination velocity could also increase and reduce the effectiveness of the greater short wavelength response of the inversion layer. The UV measurements with this cell were all less than 1 ma which substantiates the possibility of a high rate of surface recombination.

These cells are somewhat stable but are of comparatively low output and have poor UV sensitivity so this phase of the work was suspended. Figure 14 shows the I_{sc} response of several of the cells.

K. Inverting Surfaces from Evaporated Layers

Previously the cells with temporary high output have been obtained with a sodium silicate layer deposited by spinning after the solution has been applied to the cell. This method of application has a mild reaction to the surface and perhaps another method of application would create the same effect but with stability. Therefore, three cells from a batch of cells with aluminum top contacts were chosen and a coating of sodium silicate was provided by evaporation. Cells with etch times of 20, 40, and 100 seconds were used. The coating on the 20 and 40 second cells was too heavy, being closer to the evaporation source, and the output decreased by the coating on the 100 second cell was thinner and the output increased from the original 3.9 ma to 98 ma when exposed to artificial white light and from .04 ma to 3.7 ma when exposed to the UV black light source. No heat was applied to the cell during the evaporation or afterwards. This shows a definite indication of a strong inversion being created because of the presence of the evaporated sodium silicate layer. Because no water vapor was present in the evaporation or on the surface of the cell when in the evaporation, this becomes equivalent to spinning on a solution of sodium silicate and driving the water out with heat.

Because of this success, three other cells were chosen from the batch of cells processed above and sodium silicate evaporated on the surface. The 50 sec etch cell increased from 48 ma I_{sc} to 110 ma for white light and increased from .52 ma to 3.8 ma for UV. The 60 second cell increased from 40 ma to 105 ma and .46 ma to 2.9 ma; likewise, the 70 second cell from 6.4 ma to 50 ma and .1 ma to 2.2 ma. Thus, the pattern seems to be consistent.

One day later, however, the cells showed a definite decrease in output as the following table shows:

<u>Cell</u>	<u>Isc white</u>	<u>Isc UV</u>
50	96	1.7
60	63	1.6
70	28	1.6
100	48	3.1

It seems that even though high performance is gained without heating the cell, the same deterioration mechanism plagues the evaporated sodium silicate cell as well as the spun on sodium silicate cell.

In an attempt to prevent this deterioration, a number of different overcoatings were applied to the cells after a sodium silicate evaporation. Cells 6G and 7G were given a sodium silicate evaporation followed by an evaporated pyrex glass coating. The results follow.

<u>Cell No.</u>	<u>Isc</u>		<u>Isc</u>	
	<u>Before Evaporation</u>		<u>After Evaporation</u>	
	<u>White</u>	<u>UV</u>	<u>White</u>	<u>UV</u>
6G	3.8	.10	105	4.0
7G	7.4	.18	108	4.0

To ascertain the effect of pyrex glass alone, an evaporation of pyrex was made on cells 2G and 3G with no prior sodium silicate evaporation.

<u>Cell No.</u>	<u>I_{sc}</u>		<u>I_{sc}</u>	
	<u>Before Evaporation</u>		<u>After Evaporation</u>	
	<u>White</u>	<u>UV</u>	<u>White</u>	<u>UV</u>
2G	10	.18	13	1.2
3G	13	.30	16	1.3

Cells 6G and 7G were measured after one day. White light I_{sc} was 9.5 ma and 5.3 ma and UV I_{sc} was .32 ma and .13 ma, respectively. Again, a decrease that shows the instability of the silicon-sodium silicate interface.

An attempt to stabilize the cell by encapsulating in a clear plastic resin was made. Cell number 1H, whose output was 2.5 ma, grew in output to 105 ma when an evaporation layer of sodium silicate was applied. After spinning a layer of liquid plastic resin the output fell to 2.9 ma. Cell 2H was similarly treated and the I_{sc} values were 3.6 ma, 110 ma, and 4 ma, respectively. Evidently the casting resin has some effect directly with the cell.

A try was made to embed sodium ions in a layer of glass by first evaporating a layer of sodium chloride on a cell and then evaporating a layer of pyrex glass. Cells 5H and 6H were used for this experiment and no increase in the cell output was observed.

Sodium silicate was evaporated on cells 7H and 8H followed in the same pump-down by a pyrex evaporation. Cell 7H went from 3.0 ma to 48 ma, and cell 8H went from 4.0 ma to 80 ma. A day later the outputs were 12 ma and 4 ma, respectively.

Another group of wafers was processed to help in this investigation (Group K). A coating of sodium silicate followed by a coating of CaO was applied to the surfaces of two Mesa Cells. Before evaporation the output of cell 1K was 4.8 ma I_{sc} , .43 volts V_{oc} , .1 ma UV, and the output of cell 2K was 5.1 ma I_{sc} , .42 volts V_{oc} , .07 ma UV. After evaporation the outputs rose to 22 ma, .43 volts, .7 ma UV and 40 ma, .46 volts, .8 ma, respectively.

Cr_2O_3 was evaporated on cells 3K and 4K with no increase in output. Sodium borate (borax), $Na_2B_4O_7$, was evaporated onto cells 5K and 6K, and the output rose from 6.4 ma I_{sc} to 46 ma on cell 5K and from 4.6 ma to 60 ma on cell 6K. The ultraviolet response increased accordingly. Unfortunately, these cells were unstable also and decayed to 3.4 ma and 4.0 ma I_{sc} over a weekend. The cells were given a heat treatment (660°F for 30 sec) and the output increased to 50 ma for 5K and 80 ma for 6K but decayed to 10 ma in a short time. Thus, borax seems to cause an inverted surface but suffers from the same decreases found with sodium silicate.

Cell number 10K was given an evaporated coating of sodium silicate and then coated with silicon monoxide. The I_{sc} output rose from 5.6 ma, but decayed to 20 ma overnight. The SiO does not protect the sodium silicate from deterioration.

Further evaporation involving sodium borate covered with various glasses were tried but, although some of them reached high output, all of them decreased with time.

A series of experiments with sodium silicate and various evaporated overlays was completed. Since a high output is achieved when sodium silicate is evaporated on the surface of a mesa wafer, an encapsulating coating evaporated in the same pump-down should tend to keep the output

steady. A group of 12 cells was processed (Group N) to test the encapsulating properties of some glasses. The materials evaporated and how the cells were handled will be itemized below and a final table of the short circuit current as a function of the day measured will be presented after that.

Group N Cells

2x2 p wafers, mesa type, aluminum contacts, n diffusion 945°C
20 min, Si etch 100 sec.

Cells 1N and 2N were given a sodium silicate evaporation followed by a microscope glass evaporation. They were sintered for 2 min at 400°C after the evaporation, and then cooled slowly (400°C to 30°C in 15 min).

Cells 3N and 4N were given a coating of sodium silicate followed by microscope slide glass and sintered similar to cells 1N and 2N.

Cells 5N and 6N received an evaporation of sodium silicate and a 3 min evaporation of microscope slide glass, sintering was the same as other cells.

Cells 7N and 8N were coated with sodium silicate followed by a coating of pyrex; sintering was the same.

Cell 9N was coated with sodium silicate but no glass overlay, with sintering the same.

Cells 10N and 11N were coated with evaporated sodium silicate and no glass. Cell 10N was sintered prior to evaporation and cell 11N after evaporation. This experiment was performed to see if the time of sintering would alter the stability of the cell.

Cell 12N was given a coating of sodium borate with no glass. Sintering followed the evaporation, 400°C for 2 minutes.

The following table shows results on N group of cells. All readings are I_{sc} in ma.

Date: August 1974										
	F	S	M	T	W	Th	F	M	T	W
Cell No.	16	17	19	20	21	22	23	26	27	28
1N	26	22								
2N	65	65		(Heated) 101						
3N		92	68							
4N		78	80	80	72	66	66	62	62	57
5N			92	92	92	75	75	74	74	52
6N			91	90	82	72	72	42	42	34
7N				11						
8N				14						
9N				78	82	15	11	10		
10N					100	66	40	28		
11N					105	94	54	28		
12N					90	22	19	18		

L. Contaminated Oxide on Mesa Cells

An attempt to apply or grow an oxide coating and contaminate with sodium was made with little success. A coat of SiO_2 was spun on using a commercial Emulsitone product. After appropriate heat treatment, the cell was placed on a hot plate covered with a pyrex dome. A flow of sodium contaminated steam was introduced through the top of the dome. After a 2-1/2 hour exposure at a hot plate temperature of 600°F , the cell output increased to 13 ma from an original 3 ma. The cell was dipped into water to see if the same degradation was present as the sodium silicate cells, and no decrease was noted. After another hour on the vapor hot plate the I_{sc} reached 15 ma. After another 6 hours, the output did not increase at all. Thus, an enhancement of the cell occurred but not nearly what is needed.

A evaporated coating of SiO was applied to a cell whose original I_{sc} output was 17 ma. It increased to 30 ma. After 1-1/2 hours exposure to the steam-heat, the output decreased to 11 ma. Another cell was chosen with an output of 85 ma. It was exposed to the sodium steam for one hour at 300°F . A visible coating was observed on the surface (presumably salt). A coat of SiO was applied and the output went to 110 ma. After heating to 500°F , the I_{sc} dropped to 100 ma. This latter experiment was performed to assure the presence of salt in the SiO and if the salt was applied before the SiO , it could only escape through the SiO layer.

M. Tin Oxide on n Wafers

Since there was some indication that tin oxide produced from the decomposition of stannous chloride (SnCl_2) will create a stable inversion layer when applied to a Mesa Cell, another method of applying SnO_2 was tried. Tin oxide produces a transparent coating that is slightly conducting. This coating was used by our laboratory previously, to obtain a transparent conducting layer for the transparent electrode cell. This tin oxide was applied by passing vapors of stannic chloride (SnCl_4) and wet oxygen over a heated silicon wafer. The gases react at the hot surface and leave a deposit of tin oxide.

When tin oxide was deposited on a p wafer Mesa Cell using this method, no significant increase in output was observed. When a deposit was made on a base p silicon wafer, however, a small (2 ma, .2 v) response resulted, but with opposite polarity to that expected. That is, the bottom of the p wafer was negative and the tin oxide layer positive. This is reverse polarity if we assume the tin oxide to provide an n-type layer.

A number of p over n mesa inversion cells were fabricated. A group of four individual cells was processed with the following schedule:

1. Clean wafers (n - 2-4 ohms cm, 1" dia)
2. Predep diffusion, 1160°C, 5 min, BN source
3. Drive in, 1050°C, 15 min
4. Evaporate metal front surface
5. Photoresist finger pattern
6. Etch metal and silicon past junction
7. Evaporate back contact
8. Deposit SnO_2
9. Test

All of the cells were measured before the SnO_2 growth and a short circuit current of around 1 ma and an open circuit voltage of about .3 volts was found for each cell. Aluminum contacts were used for this group.

The results for this group (III) are found below:

<u>Cell No.</u>	<u>I_{sc} (ma)</u>	<u>V_{oc} (volts)</u>	<u>UV (ma)</u>
III A	57	.42	4.0
III B	37	.36	2.0
III C	47	.40	3.0
III D	72	.42	4.0

Cell No. III B was given a thinner coat of SnO_2 than the rest, and the lower output can be attributed to it. The SnO_2 slopped over the edge during deposition, but this was removed with HF. The UV response indicates a shallow junction such as an inversion layer.

Another group processed that gave interesting results was Group V. Group V consisted of four cells, two with aluminum contacts (A and B) and two with Ti-Ag contacts (C and D). They were diffused at 1050°C for five minutes and driven in at 1050°C for ten minutes. Cell V-A was given a coat of SnO_2 that brought the cell output to 32 ma I_{sc} with .41 volts, V_{oc} and UV of 3 ma. Cell V-B started with 15 ma due to a thin coating of SnO_2 , but moved to 35 ma on the second coat and 33 ma on the third. The open circuit voltage was .43 volts and the UV response at 3.7 ma. Cell V-C went from 40 ma I_{sc} to 18 ma on the second coat. Cell V-D was coated first with a very thin coat bringing the cell output to 26 ma I_{sc} , .43 volts V_{oc} and 3.0 ma UV. A second coat yielded 31 ma, the third 31 and the fourth 23 ma. The open circuit voltage decreased slightly as successive coats were applied as did the UV response.

It is apparent that the tin oxide thickness affects the output, increasing to a maximum and then decreasing. The maximum seems to yield a blue color so the maximum is probably a combination of surface state density, absorption in the oxide and antireflection coating.

Another batch of cells was fabricated and a fresh solution of SnCl_4 was used to deposit the tin oxide. The output of these cells was higher than the others. The results were as follows:

<u>Cell</u>	<u>I_{sc} (ma)</u>	<u>V_{oc} (volts)</u>	<u>UV (ma)</u>
A	105	.46	3.7
B	65	.42	3.8
C	98	.46	3.1
D	105	.46	3.0
E	105	.40	2.5
F	76	.40	2.5

A measurement of these cells seven days later, showed the following decreases:

<u>Cell</u>	<u>I_{sc} (ma)</u>	<u>V_{oc} (volts)</u>	<u>UV (ma)</u>
A	94	.40	3.7
B	37	.40	3.1
C	82	.40	3.5
D	56	.43	2.9
E	82	.29	2.4
F	47	.26	2.4

Every cell in this batch suffers some significant decrease. It is interesting to see that although the total response to tungsten light decreased, the response to ultraviolet remained quite steady.

The higher output on these cells is probably due to a change in the method of depositing SnO_2 . Heretofore the reaction tube had been open and exposed to the air, whereas the tube was closed when the deposition was started with this batch.

It was noticed that the contact patterns were changing in appearance and some of them were lifting, so in order to check whether the contact SnO_2 coating or its method of deposition was affecting the contact and causing all or part of the deterioration of the cell, two cells were fabricated of the non-mesa variety similar to the contaminated oxide cell but using tin oxide on n wafers instead of sodium ions in an oxide layer. The fabrication procedure was:

1. Grow clean oxide on wafer.
2. Etch finger pattern windows in oxide.
3. Diffuse n.
4. Remove oxide.
5. Deposit SnO_2 .
6. Etch finger pattern over diffusion in SnO_2 .
7. Deposit metal.
8. Etch metal in finger pattern.

Steps were also included to prepare the back of the wafer.

Thus a cell is created with the tin oxide creating the inversion layer, but the Ti-Ag contact is not in contact with the SnO_2 , neither was the metal present while the SnO_2 was deposited. These two cells were designated as Group XVI and the outputs were:

<u>Cell</u>	<u>I_{sc} (ma)</u>	<u>V_{oc} (volts)</u>	<u>UV (ma)</u>
A	40	.41	1.0
B	43	.38	1.2

These cells were observed for two months and no change in any of the values above was noted, neither was there any visible change in the appearance of the contacts on the cell. Thus, stable mesa cells of the p or n variety could be fabricated if the contact versus tin oxide coating method problem could be solved.

N. Incremental Etch Experiment

A number of wafers was prepared with standard processing consisting of a phosphorous diffusion at 945°C for 20 minutes, a Ti-Ag metal deposition, and a photoresist spin and develop using the 20 finger mask. Each cell was etched at different times so different mesa depths were obtained. This allows a look at the cell response as the diffusion becomes shallower and the surface nearer the junction. An increased ultraviolet response may result because of the removal of the dead layer and the existence of the junction electric field nearer the surface. Another reason for a proposed greater ultraviolet response is the etch removal of some of the imperfections created by sawing during the slicing operation to create the wafer.

The results of one of these experiments showed an increase in power output for etched cells over the non-etched cells. One must remember that the diffusion was done at 945°C for 20 minutes and yields a junction depth of approximately a micron which produces a cell of lower output than the conventional shallow junction type. The etched cells, although higher

in power than the non-etched ones, were still lower in output than the conventional "blue" cells used for space applications.

Figure 15 shows a number of I-V curves labelled with the time in seconds the cell was etched. A conventional cell is also shown to compare the I_{sc} values show a rise and then a definite fall, peaking at about 1 second. The open circuit voltages hold steady until the lower I_{sc} 's are obtained.

Each of the cells that received an etch was coated with a spun-on layer of sodium silicate. The purpose of this coating was to see if a combination mesa cell could be developed wherein the n diffusion is etched back to yield a weak diode and therefore a weak photon collector and yet have a significant increase in power output by creating an inversion layer at the surface. Figure 16 shows the same cells as in Fig. 15, but with a coating of sodium silicate. The output of most of the cells increased by about 20%. The output of the 2-1/2, 3, and 3-1/2 second etches, however, increased significantly as shown in Figures 17, 18, and 19, respectively. The 3 second cell had an added heat treatment that caused the output to increase even more.

It is obvious that the addition of the sodium silicate caused an increase in each cell. For those of higher output the function of this layer was perhaps not much more than an antireflection coating. But to the others, an increase in the p-n collection efficiency is noted. The inversion layer adds to the weak diffused junction and both of them are responsible for the output as seen. A change of I_{sc} from 35 ma to 61 ma

for the 3 second etch cell after the sodium silicate, represents more than an antireflection coating, and the further increase to 97 ma for this cell when heated is further evidence that an inversion layer is present.

Another experiment similar to the one just described was completed. An etch consisting of 45 ml acetic acid, 16 ml nitric acid and 4 ml of hydrofluoric acid was used to etch into a junction formed on the surface of a 2x2 cm wafer at 945°C for 20 minutes. The 20 finger pattern contact was titanium-silver. Eleven cells were used in the sun (Group A), etched in increments of 5 seconds ranging from 0 to 50 seconds.

After the deposition of a Ti-Ag back contact and a sintering operation, the cells were measured for I_{sc} under a tungsten light. The following data were obtained:

<u>Time of Etch (sec.)</u>	<u>I_{sc} (ma)</u>
0	80.0
5	92.0
10	39.0
15	5.0
20	2.4
25	4.2
30	4.2
35	3.5
40	3.1
45	2.7
50	3.2

One coat of sodium silicate was spun on the surface and the output was changed:

<u>Time of Etch (sec.)</u>	<u>I_{sc} (ma)</u>
0	93.0
5	110.0
10	92.0
15	50.0
20	1.0
25	3.0
30	4.0
35	2.5
40	4.5
45	(eliminated)
50	4.0

After heat treating to 700°F:

<u>Time of Etch (sec.)</u>	<u>I_{sc} (ma)</u>
0	86.0
5	94.0
10	94.0
15	70.0
20	2.0
25	24.0
30	18.0
35	18.0
40	4.0
50	5.0

Two days later with no heating, the outputs were:

<u>Time of Etch (sec.)</u>	<u>I_{sc} (ma)</u>
0	93.0
5	110.0
10	40.0
15	4.0
20	2.0
25	3.0
30	3.0
35	2.5
40	3.0
50	3.0

Significant changes have occurred for some of these cells. The change in the 0 and 5 sec. cells is probably due mainly to an antireflection coating. The change in cells 10, 15, 25, 30 and 35 sec. is probably due to an inversion layer induced in the surface by surface states created by the sodium silicate. Notice again there is a decline of output over time for the surface treated with sodium silicate. Even the fresh spin-on deteriorated although no heat was applied. It is interesting to see the deterioration ended at the original value of output except for the high output cells whose increase was due to the antireflection properties of sodium silicate.

Another group of cells (Group B) was processed the same as Group A, only the etch times were closer together to get a more detailed look at the region of high output around the 5 sec. etch. The list on the following page shows the change in I_{sc} output after each operation.

Again these data show a definite increase when the sodium silicate is introduced and especially after heating. The increase ratio for each etch time is shown in the second list on the following page.

<u>Time of Etch (sec.)</u>	<u>After Sintering</u>	<u>1 coat Sodium Silicate (ma)</u>	<u>700°F Heat (ma)</u>	<u>5 Days Later (ma)</u>
0	74.0	86	94	86.0
1	84.0	102	113	108.0
2	80.0	96	113	105.0
3	82.0	105	115	110.0
4	82.0	105	113	113.0
5	75.0	100	105	100.0
7	10.0	15	50	11.0
10	26.0	45	76	33.0
12	4.0	10	30	7.0
13	3.2	11	20	6.0
15	4.0	7	28	4.5

<u>Time of Etch (sec.)</u>	<u>Ratio of Change (%)</u>
0	1.27
1	1.35
2	1.41
3	1.40
4	1.38
5	1.53
7	5.00
10	2.90
12	7.50
13	6.30
15	7.00

It looks as though the heated sodium silicate had an effect on even the shallower etch cells greater than would be expected from an anti-reflection coating unless the sodium silicate is superior to the silicon monoxide used on conventional cells. An indication of a contribution above antireflectivity is evidenced in observing that the output decreases in time during the five days after heating. This is typical of a cell whose output depends somewhat on an induced layer created by a contaminated insulating layer on surface states. Thus perhaps an inversion is being formed at the

surface of even the shallower mesas and enhancing the collection of the photon produced carriers, maybe in the shorter wavelengths. A definite increase can be seen for those cells etched beyond the n diffused layer or close to it. This high increase is due to the formation of an induced junction.

An experiment was performed to gauge the antireflection properties of sodium silicate. A V-I curve of a conventional space cell coated with SiO was taken, and subsequently, the SiO antireflection coating was removed, and another V-I curve was taken. Sodium silicate was applied by spinning like the other cells, and a V-I curve taken of the result. The curves are shown in Fig. 20 showing all three for comparison. The output of the cell fell from 116 ma I_{sc} to 78 I_{sc} after the coating was removed with hydrofluoric acid. This is a decrease of .67 or an increase of 1.49 if the effectiveness of the SiO is wanted. After the coating of sodium silicate was applied, the output increased to 98 ma, an increase of 1.26. Thus, the conclusion can be reached that the sodium silicate is not as effective as the silicon monoxide when used as an antireflectant. This experiment lends credence to the argument that an inversion layer is helping with the output on the shallower mesa cells.

Several other groups of cells were etched incrementally and the results observed. An interesting group was Group "D". This was a group of eight cells etched with an even slower etch than before using 60 ml acetic acid, 16 ml nitric acid, 4 ml HF. The increment was 10 sec. starting at 20 sec., and ending at 100. The 60 sec. cell was removed for another experiment. The ultraviolet response was measured for this group.

This was done by placing an ultraviolet "black light" fluorescent tube near the surface of the cell. The ultraviolet radiation was weak but enough to give significant results. For comparison, a conventional cell will respond to this "black light" source with a response of 1.5 ma I_{sc} .

The following lists show the results obtained.

Etch Time (sec)	After Sinter		After Sodium Silicate	
	White Light I_{sc} (ma)	Ultraviolet I_{sc} (ma)	White Light I_{sc} (ma)	Ultraviolet I_{sc} (ma)
20	84.0	.30	92	.52
30	85.0	.30	92	.57
40	85.0	.28	92	.55
50	64.0	.35	96	.62
70	2.6	.02	8	.80
80	3.8	.10	12	1.30
90	1.5	.02	2	.02
100	8.7	.20	40	.9

Etch Time (sec)	After 700°F		After 1 Day	
	White Light I_{sc} (ma)	Ultraviolet I_{sc} (ma)	White Light I_{sc} (ma)	Ultraviolet I_{sc} (ma)
20	115	2.6	110.0	.51
30	115	2.3	110.0	.58
40	110	3.3	105.0	.59
50	120	3.5	98.0	.52
70	60	3.4	3.4	.03
80	71	3.5	3.1	.06
90	7	.9	2.0	.02
100	98	3.5	34.0	1.00

From these data we see the same trend as in the other groups. There is a significant increase after the sodium silicate is applied and an increase, usually much bigger, when the cell is heated and then the decrease in time due to unknown causes. The interesting part of these data, however, is the change in response to the UV light indicating a greater sensitivity to the short wavelengths creating pairs at the surface. Since this is where the inversion layer is, the stronger the response to UV, the stronger is the inversion layer. This could be a good indication of the existence and extent of an inverted surface. Cells etched for 20, 30, and 40 sec. decreased but little for the day after being heated when exposed to white light, but changed greatly when exposed to UV light. Conventional cells have a UV output of about 1.5 ma.

The cell that was etched for 100 sec. is interesting. Some inversion existed before the sodium silicate spin and jumped to 40 and 98 when the spin and heat was applied, and although the original output at 8.7 ma was one tenth of the top three, the UV response was only two thirds of the top three, a strong evidence for an inversion layer.

IV. CONTAMINATED OXIDE CELL

The contaminated oxide cell is a stable cell. It is not fabricated like the mesa cell. The inversion layer depends on the presence of positive ions in the oxide rather than the creation of surface states at the silicon surface. Contaminated oxide cells produced a year ago are still steady.

The contaminated oxide is grown by bubbling oxygen through a water solution containing a sodium compound. A small amount of the sodium goes over with the steam and provides the ions in the oxide for inversion.

Several successful runs were made with the contaminated oxide cell. Run No. Na 4 consisted of four cells. These were fabricated with the following procedure:

1. Grow contaminated oxide on p wafer.
2. Cut finger pattern into oxide.
3. Diffuse n type into window.
4. Deposit metal.
5. Etch metal into finger pattern.
6. Process back of wafer for good contact.

Aluminum was used for the contact for this run. The results were:

<u>Cell</u>	<u>I_{sc}(ma)</u>	<u>V_{oc}(volts)</u>	<u>UV (ma)</u>
1	16	.47	.7
2	20	.45	1.0
3	27	.46	1.4
4	52	.48	2.2

These cells have been steady with no sign of decreasing. The UV response is good and the open circuit voltage is adequate.

Similar results were obtained with run No. 6. Fabrication was the same except more salt was used in the bubbler to increase the contamination in the oxide. The data taken are listed below:

<u>Cell</u>	<u>I_{sc}(ma)</u>	<u>V_{oc}(volts)</u>	<u>UV (ma)</u>
1	27	.47	1.0
2	13	.44	.4
3	---	---	---
4	17	.47	.2
5	16	.46	.4
6	48	.48	2.2

Many more runs were started but the sodium began to cause a crust on the surface of the cell and further processing was stopped on each batch. After cleaning the furnace tube and the wafer boat a clear contaminated oxide could be grown. A change in processing procedure was also initiated. Since the contaminated oxide is subjected to a high temperature for about 15 minutes during the diffusion step, some of the sodium probably escaped the oxide and left a weaker inversion region. Therefore, a step was added after the diffusion to put back some of the sodium. This extra step consisted of putting the wafer into the contaminated oxide tube again for about 5 minutes in contact with the sodium vapor.

Run No. 13 used this procedure. Ti-Ag contacts were used also.

The results are:

<u>Cell</u>	<u>I_{sc} (ma)</u>	<u>V_{oc} (volts)</u>	<u>UV (ma)</u>
1	64	.43	2.5
2	59	.43	2.4
3	59	.42	2.5
4	62	.42	2.3

A significant increase in I_{sc} was obtained over the other batches. The UV response also increased. No explanation is offered at this writing. These cells will undoubtedly be stable for at least a year.

All four of these cells were sent to JPL for evaluation. A plot of the I-V characteristics for cell Na 13-4 is found in Fig. 21.

I-V curves were taken in the sun to note any differences in response between the artificial tungsten source and the natural source. Figure 22 shows the comparison. The artificial tungsten source was adjusted to give 130 ma I_{sc} on a conventional solar cell calibrated with a standard cell to equal the short circuit current at 140 mw/cm^2 in sunlight. The curve

taken in the sunlight was adjusted to equal 130 ma I_{sc} on the same conventional cell. There is a decided difference in the response both in the short circuit voltage. The greater response to sunlight indicates a stronger sensitivity to the shorter wavelengths.

Measurements made at JPL of the spectral response of the contaminated oxide cells showed a high output in the shorter wavelengths but a definite low output in the longer wavelengths. This indicates a short lifetime in the bulk p material due to thermal quenching during processing. The low short circuit currents compared with conventional cells was due to this short lifetime. To increase the bulk lifetime, an annealing step was added to the processing procedure after the last exposure to high temperature. Since the last high temperature step is the sodium impregnation step, the cells were removed from this furnace slowly to allow crystal structure changes to occur to decrease the lifetime.

Adding the annealing step brought the short circuit current to about 100 ma instead of 60 ma. A slight increase in the short circuit current and a better curve factor was obtained by using a contact pattern with 30 fingers instead of the 20 finger pattern used above. A V-I curve showing the output of an annealed contaminated oxide cell with 30 fingers is shown in Fig. 23. A curve of a 10 ohm-cm conventional cell is also shown. These curves were taken in the sun at 118 mw/cm^2 . The maximum power of the contaminated oxide cell is 39.6 mw for 4 cm^2 . This is an efficiency of 8.4%. The conventional cell efficiency is 10%. The curve factor is equal to $39.6/53.5 = .74$. This is a significant improvement over the previous performance of the contaminated oxide cells.

The following processing steps were used to fabricate the higher output contaminated oxide cells:

1. The wafers are cleaned by scrubbing with a Q-tip. Acetone and isopropyl alcohol are used. After a deionized water rinse, the wafers are blown dry with N_2 .

2. A 50-minute oxidation at $1100^\circ C$ follows. Wet oxygen, produced by bubbling O_2 through a bubbler, is passed down the furnace tube at .3 L/min in a 3" tube. The water in the bubbler is hot. An oxide coating of about 5000 \AA is grown. A dry oxygen flow is also present at .8 L/min. Wafers are inserted and removed rapidly.

3. A standard photoresist procedure is used to cut holes in the oxide for diffusion. Pattern used is the finger pattern.

4. Diffusion occurs at $945^\circ C$ for 15 minutes. Phosphorus derived from nitrogen bubbling through $POCl_3$ is used as the dopant. The $POCl_3$ temperature is maintained at $14^\circ C$. The flowrate of N_2 through the $POCl_3$ is .2 L/min, of N_2 direct is .6 L/min and O_2 direct at .6 L/min. The wafers are inserted and removed rapidly.

5. The oxide on the wafers are then impregnated with sodium by exposing the wafer to $1050^\circ C$ for 15 minutes with sodium chloride vapor being carried down the tube with flow of N_2 . The sodium chloride is set in a boat in the tube at the edge of the furnace.

6. After the 15-minute exposure to Na vapor, the NaCl source is removed and the wafers are pulled to a temperature of $800^\circ C$ in the furnace tube. Annealing then takes place by pulling 1" per 10 minutes until outside the furnace but still in the tube. The final temperature is approximately $500^\circ C$.

7. The wafers are briefly dipped in a 10:1 ammonium fluoride (40% solution) HF etch. This removes the thin oxide in the diffusion areas but leaves about 3000 Å over the p areas.

8. A deposit of Ti-Ag is evaporated on the top surface of the wafer. Evaporation takes place at 10^{-5} mm Hg.

9. A protective wax coating is applied to the top of the wafers and are subjected to a Si etch that removes the n diffused layer from the bottom and sides of the wafers.

10. An evaporated layer of Ti-Ag is applied to the back.

11. The wafers are sintered at 600°C for 5 minutes under an atmosphere of forming gas.

V. MEASURING APPARATUS

The apparatus used to trace V-I curves of the solar cells tested is pictured in Fig. 24. A variable resistor is used to load the cell in order to obtain the V-I curve. When the variable resistor is set to zero ohms, the short circuit current is obtained. When the variable resistor approaches infinite ohms, the open circuit voltage is obtained. Either the sun or a Sylvania FBE lamp can be used as a light source for the curve tracing setup.

VI. CONCLUSIONS

The mesa cell has the advantage of a more simple fabrication process. Only one masking operation is necessary and that can be done by photolithography or applique, such as silk screening. The same etch that etches the front mesas also etches the back diffusion and the edges. Dead layers and mask damage to the surface are greatly reduced. The short wavelength response compared to other solar cells is definitely greater. If other problems with this cell could be solved, the possibility of a more

efficient cell exists. The main problem, of course, is the gross degradation of the output. So far the inversion layer has been created only by surface states and not by ionic contamination in the transparent layer. Surface states are usually unstable and therefore the cell output is unstable. Further investigation might reveal a stable surface state combination. Tin oxide on n wafers shows some promise for terrestrial applications because the deterioration appears to be in the contact rather than the inversion layer. A different procedure of tin oxide deposition or a protective coating over the contact area might produce a stable cell.

Another avenue virtually untried is the construction of a mesa cell with a contaminated transparent inverting layer. Since the metal contact is present after the etching process, high temperature depositions cannot be made and therefore a thermally grown oxide contaminated with sodium as in the contaminated oxide cell cannot be done. Lower temperature deposition with isolated ions might be a possibility. This would yield a stable mesa cell.

Encapsulation does not seem to be the answer to the instability problem. Most likely, the surface is being passivated by a thin layer of oxide that reduces the surface state density. Heating causes the sodium silicate, for instance, to penetrate this small oxide layer and set up the surface states again, only to have an oxide layer slowly form and destroy the inversion layer. Since some oxygen is present before encapsulation, the rate is slowed down, but the process proceeds anyway. Presence of water vapor acts as a catalyst to speed the rate of oxidation.

Fortunately, the ionic contaminated oxide does yield stable outputs. The fabrication steps for this cell require two photolithographic steps which is a disadvantage. Generally the output has not been as large

as for the mesa cell (80 ma I_{sc} vs. 110 ma), but recent experiments show a short circuit current of over 100 ma. This higher output is due to an enhancement in the infrared collection. Data taken at JPL on the spectrum sensitivity of the contaminated oxide cell shows a large deficiency in the long wavelengths. An annealing step was added to the fabrication of the recent cells and a greater output was obtained.

VII. FUTURE INVESTIGATION

Since a stable output is obtained with the contaminated oxide cell and the addition of an annealing step has increased the output significantly, further experiments could be done to increase the efficiency. An investigation of the annealing procedure to maximize the infrared collection would help. An investigation of other ions besides sodium to serve as the contaminate might prove fruitful. New methods of introducing the ionic contamination could be useful in reducing the complication of fabrication.

For terrestrial applications the mesa cell with tin oxide on n wafers has possibilities. It is more sensitive in the UV and could be made stable if the contact metal versus method of tin oxide deposition problem could be solved. Since radiation damage is more pronounced in n wafers, this cell would not be used for space application.

For p type wafers and mesa cells, a search for a transparent layer that would harbor isolated ions and could be applied at low temperatures (< 600°C) would allow the mesa cell to be stable and produce cells of high output.

A combination of the n layer on p diffused cell and the inversion layer cell might yield a superior cell. The n layer could be etched in the

mesa fashion, but not completely through the n layer but enough to remove some of the dead layer. A layer of inverting material is then applied and the inversion layer enhances the n diffusion already there to make it more blue and UV sensitive.

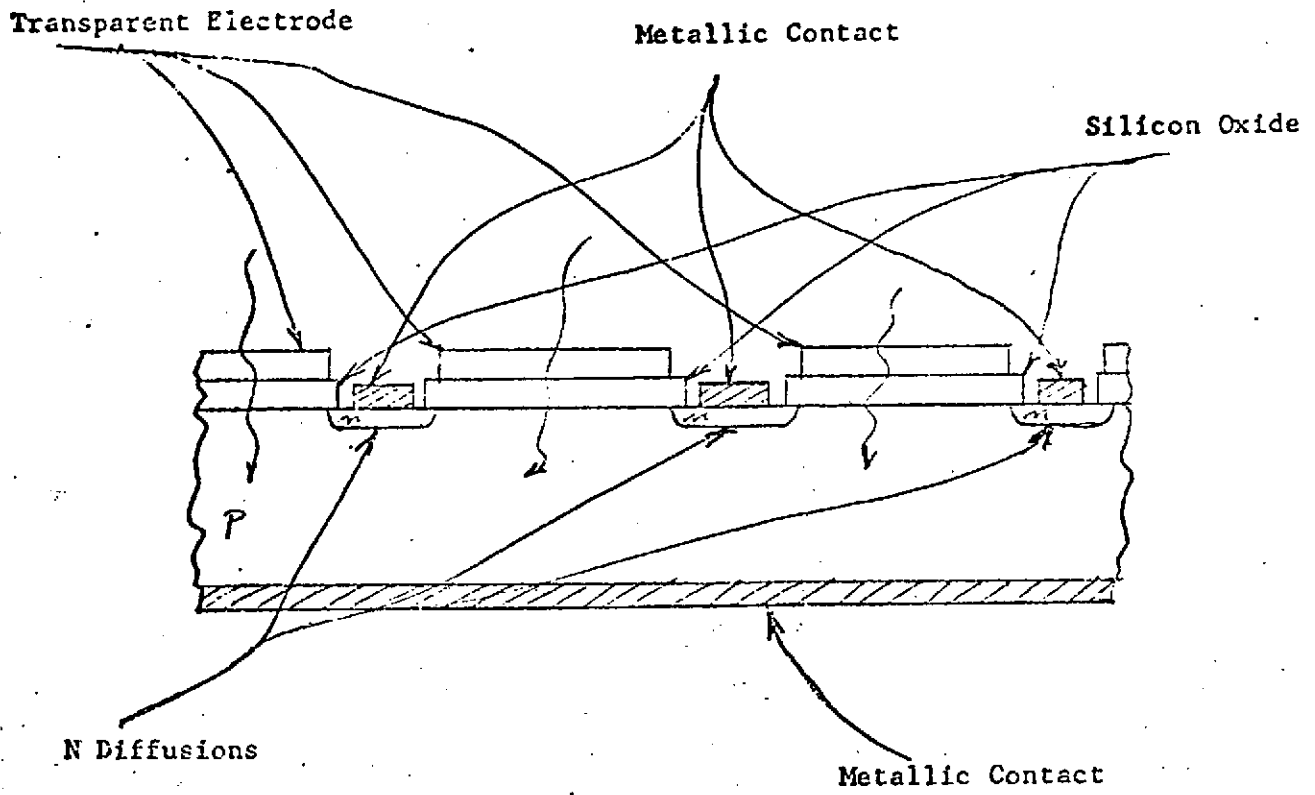


Figure 1
Transparent Electrode Cell

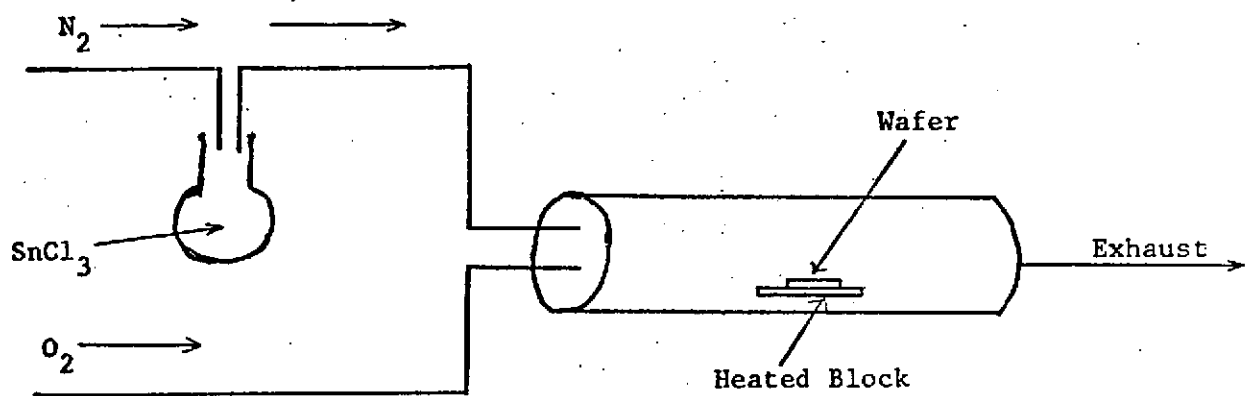


Figure 2 New Transparent Electrode Growth Apparatus

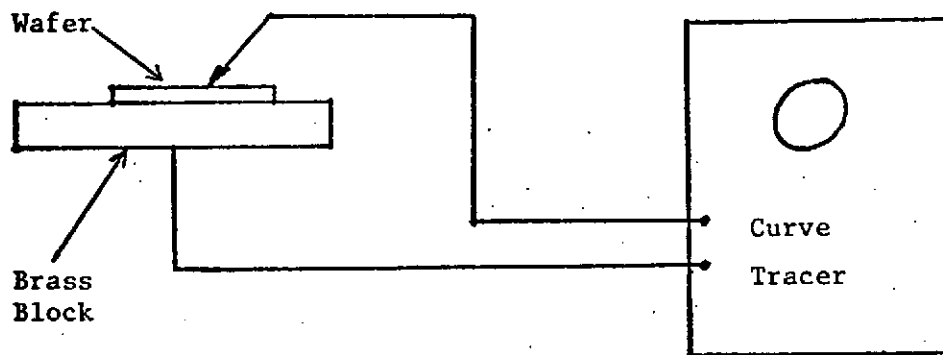


Figure 3 Breakdown Voltage Test Apparatus

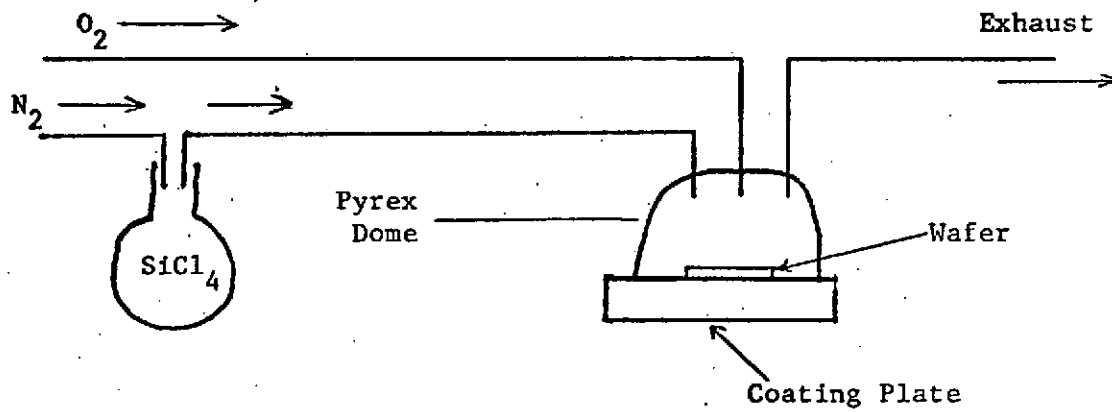


Figure 4 Apparatus to Grow SiO_2 Using SiCl_4

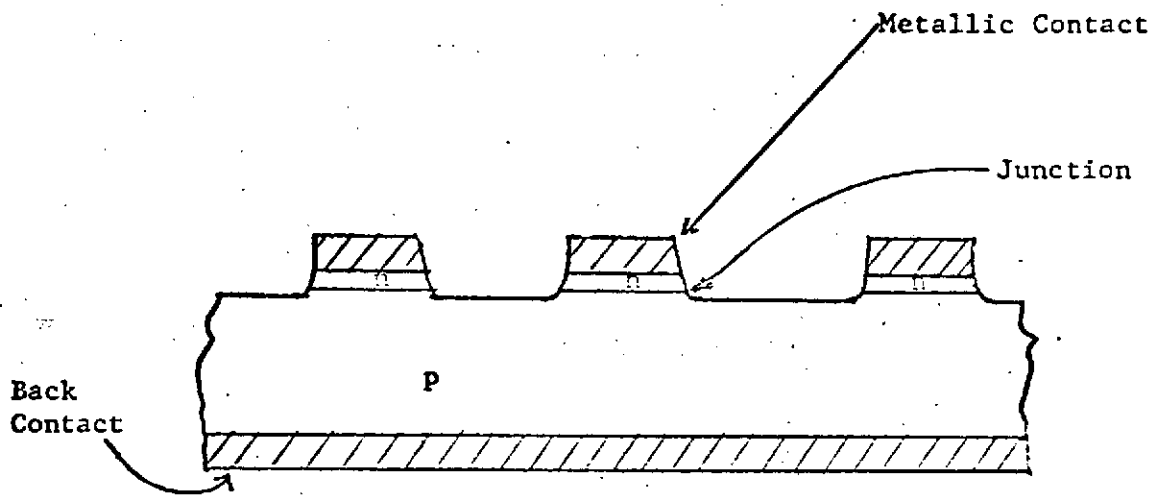


Fig. 5 Mesa Cell Without Positive Charged Layer and Inversion Layer

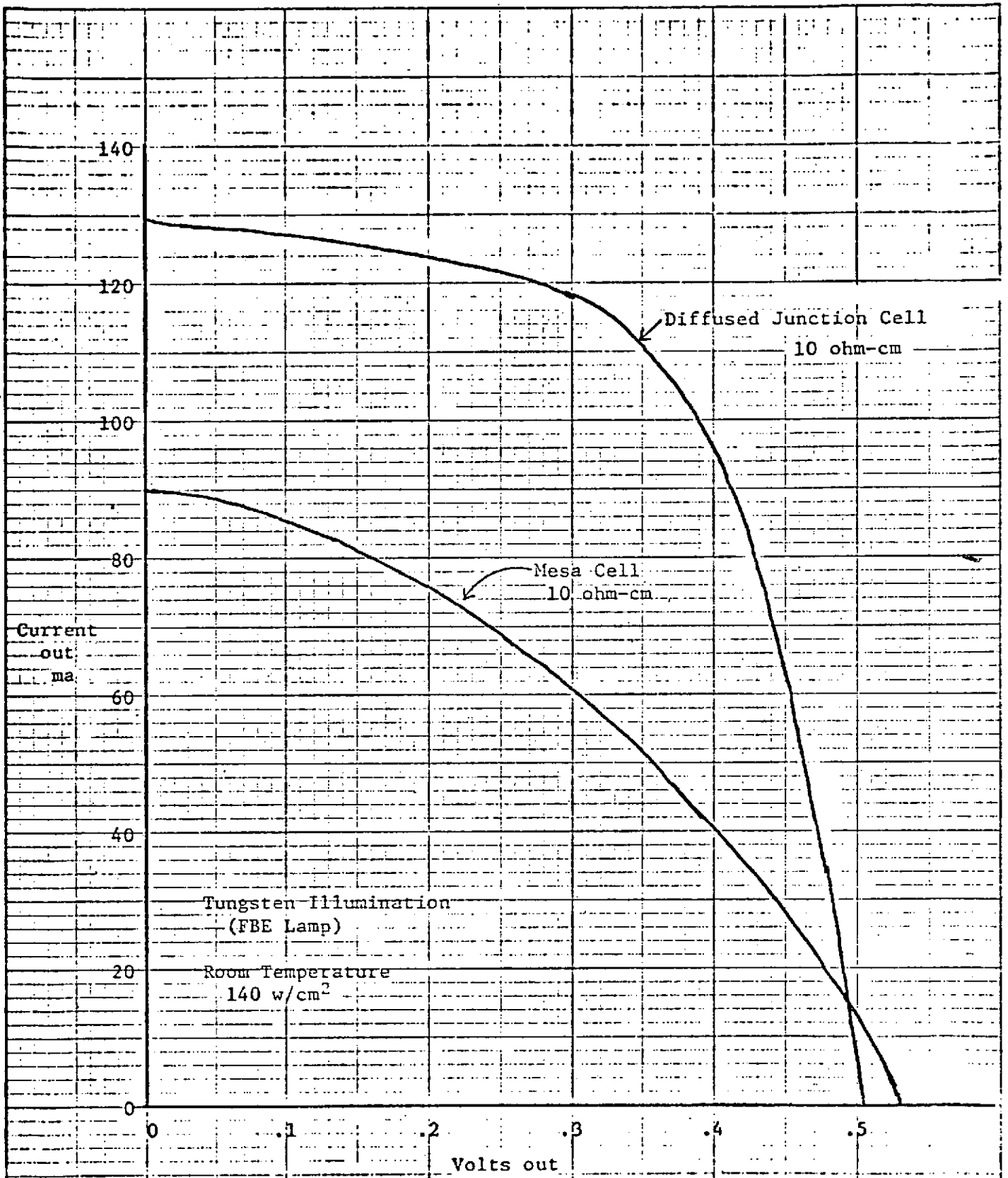
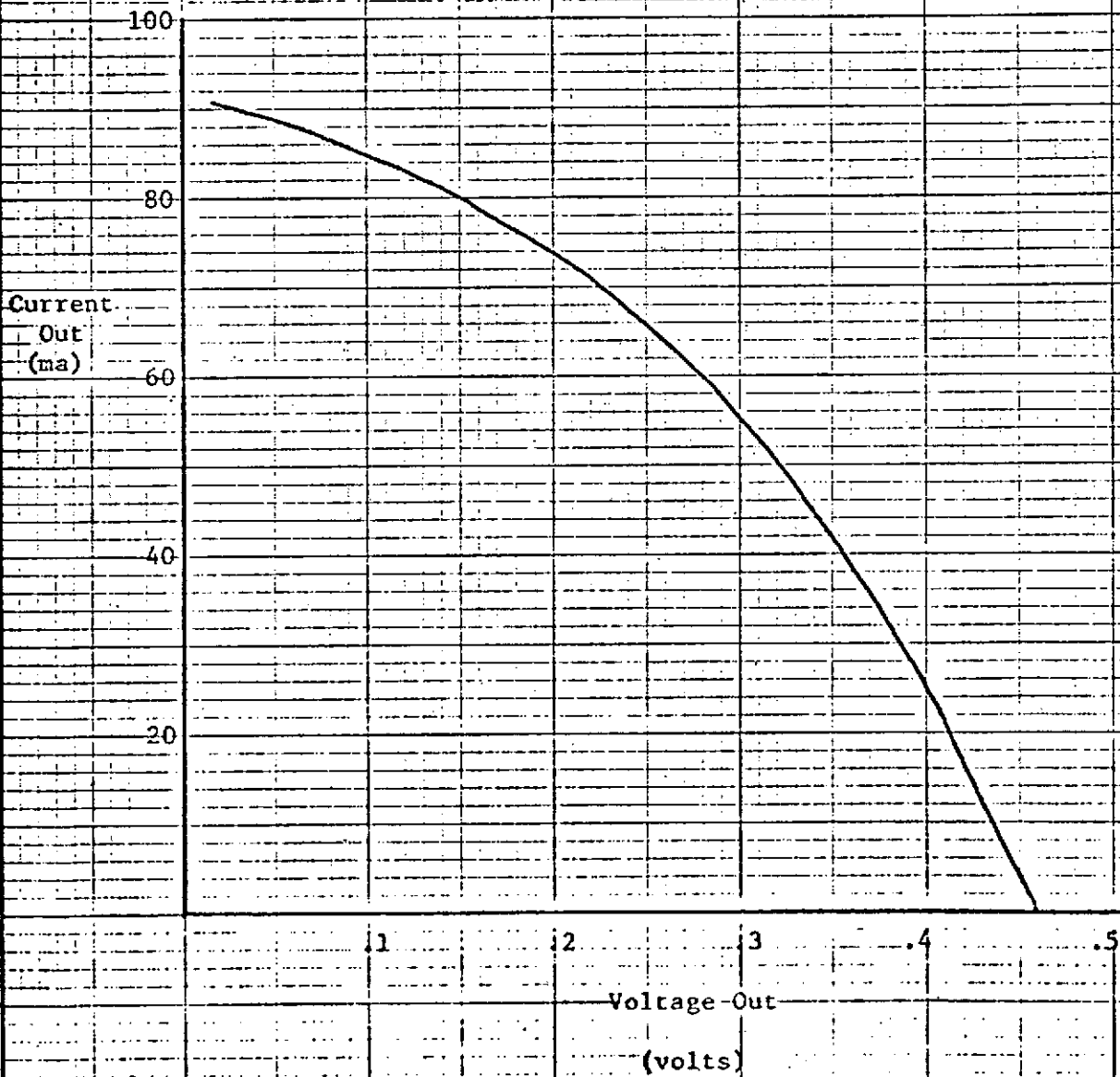


Fig. 6 I-V Characteristic Curves Comparing Conventional Cell to Mesa Cell

Figure 7

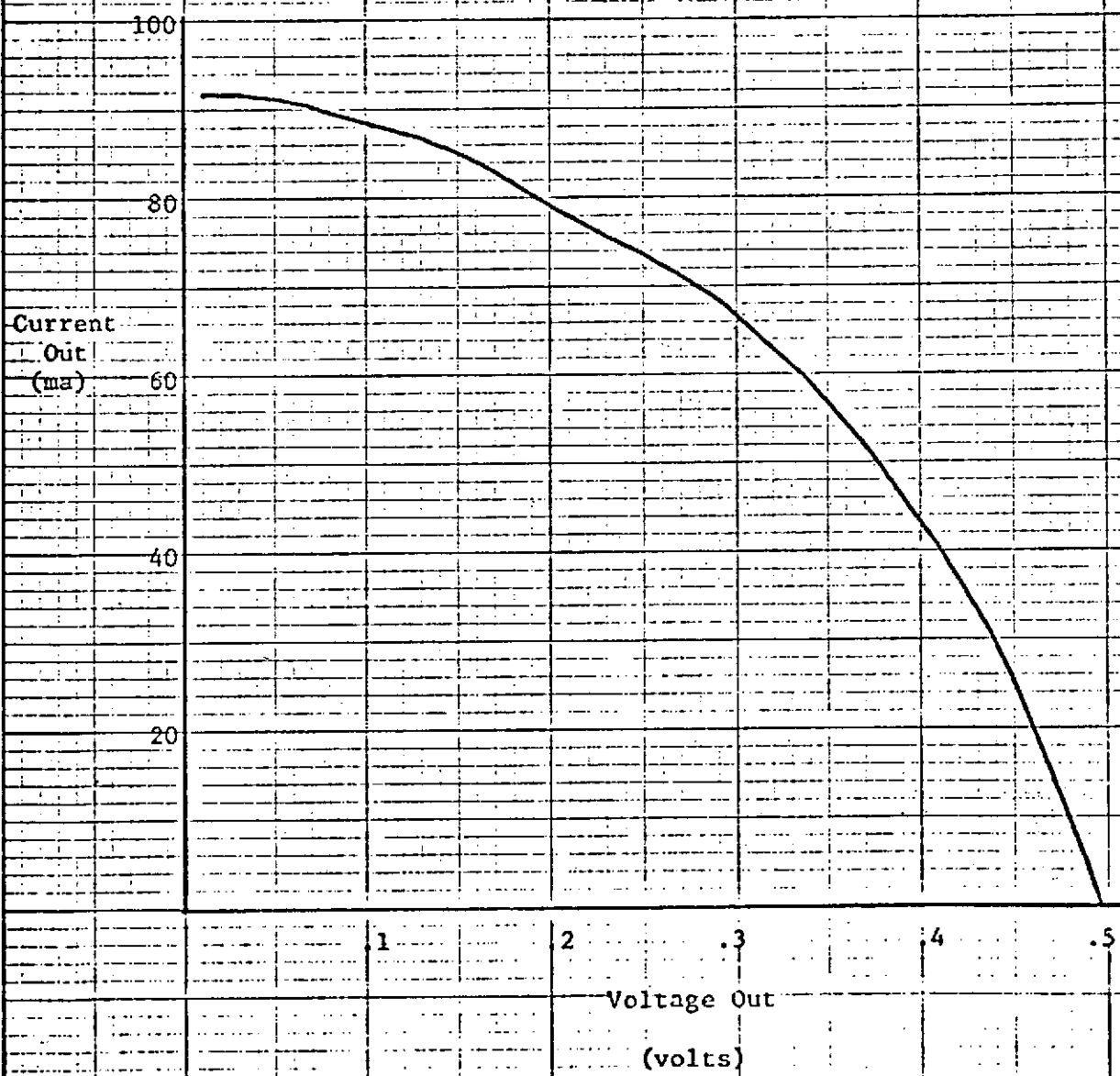
Inversion Layer "Mesa" Cell
Artificial Light
140 mw/cm² intensity
Room Temperature
Sodium Silicate Layer heated to
250°F for 5 minutes



10 X 10 TO THE INCH 40 0780
7 INCHES
UNITED STATES
UNITED STATES

Figure 8

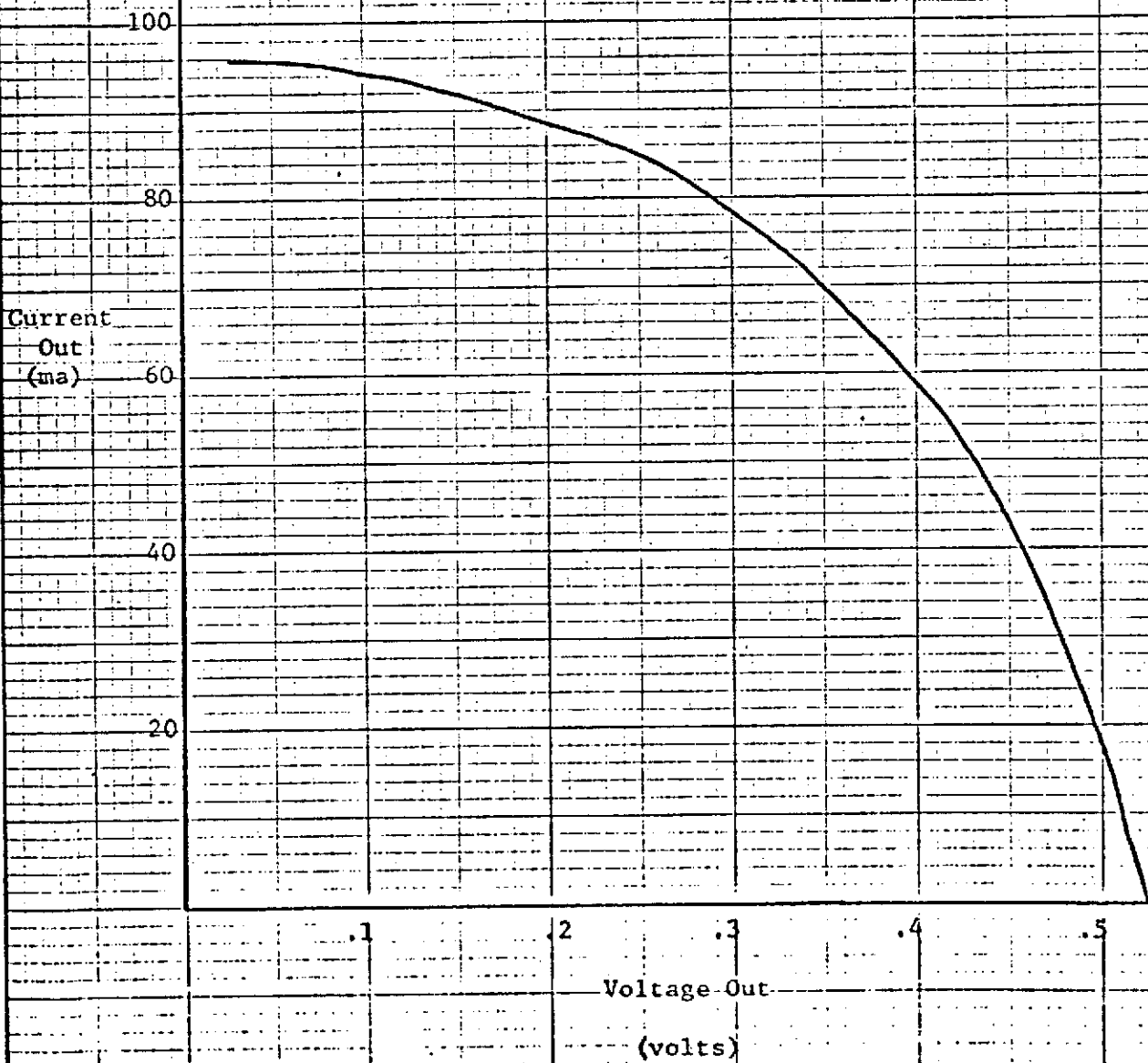
Inversion Layer "Mesa" Cell
Artificial Light
140 mw/cm² intensity
Room Temperature
Sodium Silicate Layer heated to
400°F for 5 minutes



10 X 10 TO THE INCH 46 0780
7 X 10 INCHES
MADE IN U.S.A.
KODAK SAFETY FILM

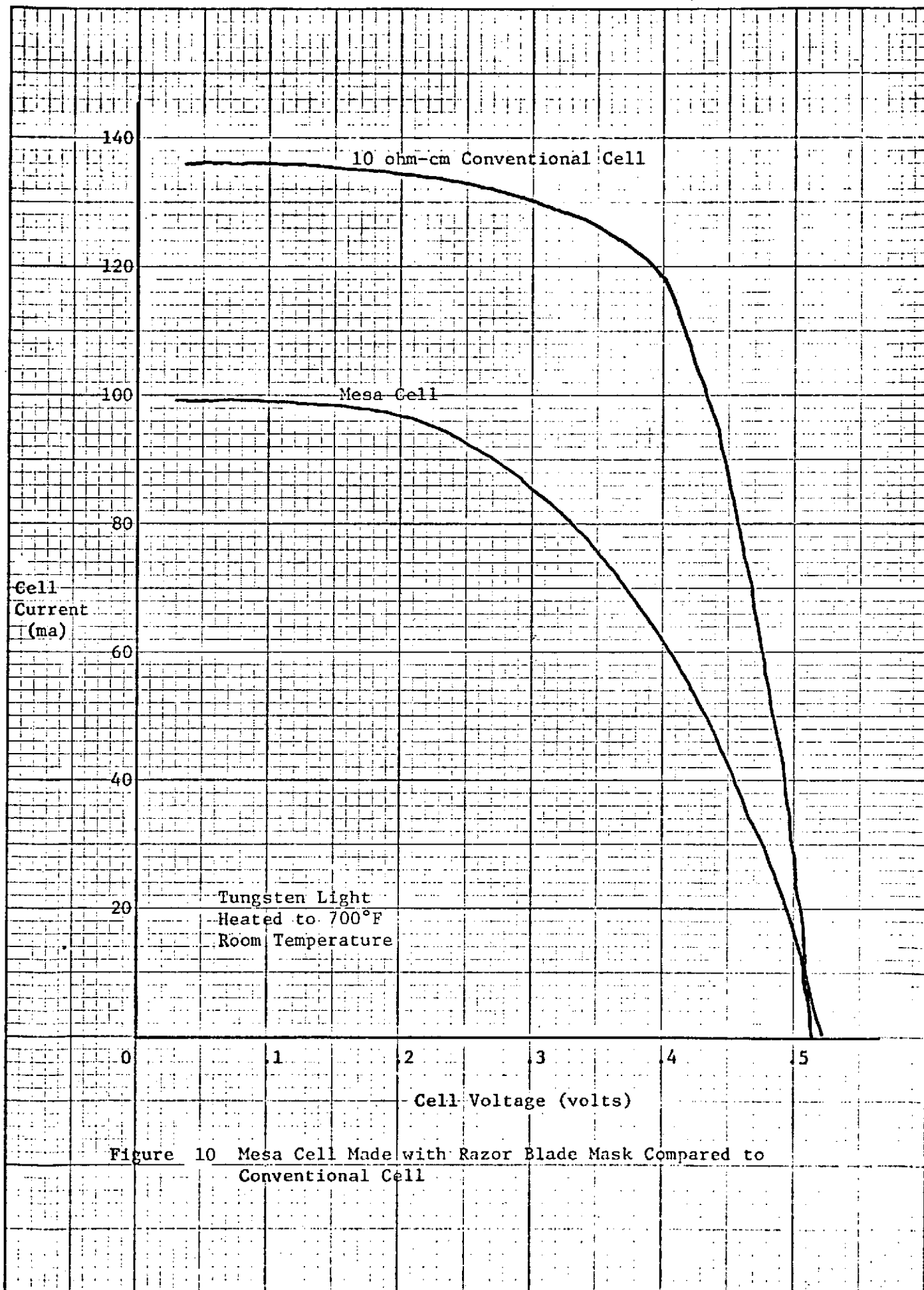
Figure 9

Inversion Layer "Mesa" Cell
Artificial Light
140 mw/cm² intensity
Room Temperature
Sodium Silicate Layer heated to
600°F for 5 minutes



7
SOCIETIES
NEUFFEL & LESSER CO.

10 X 10 TO THE INCH 46 078
KREUFFEL & ESSER CO.
U.S.



10 X 10 TO THE INCH 46 0780
KEUFFEL & ESSER CO.

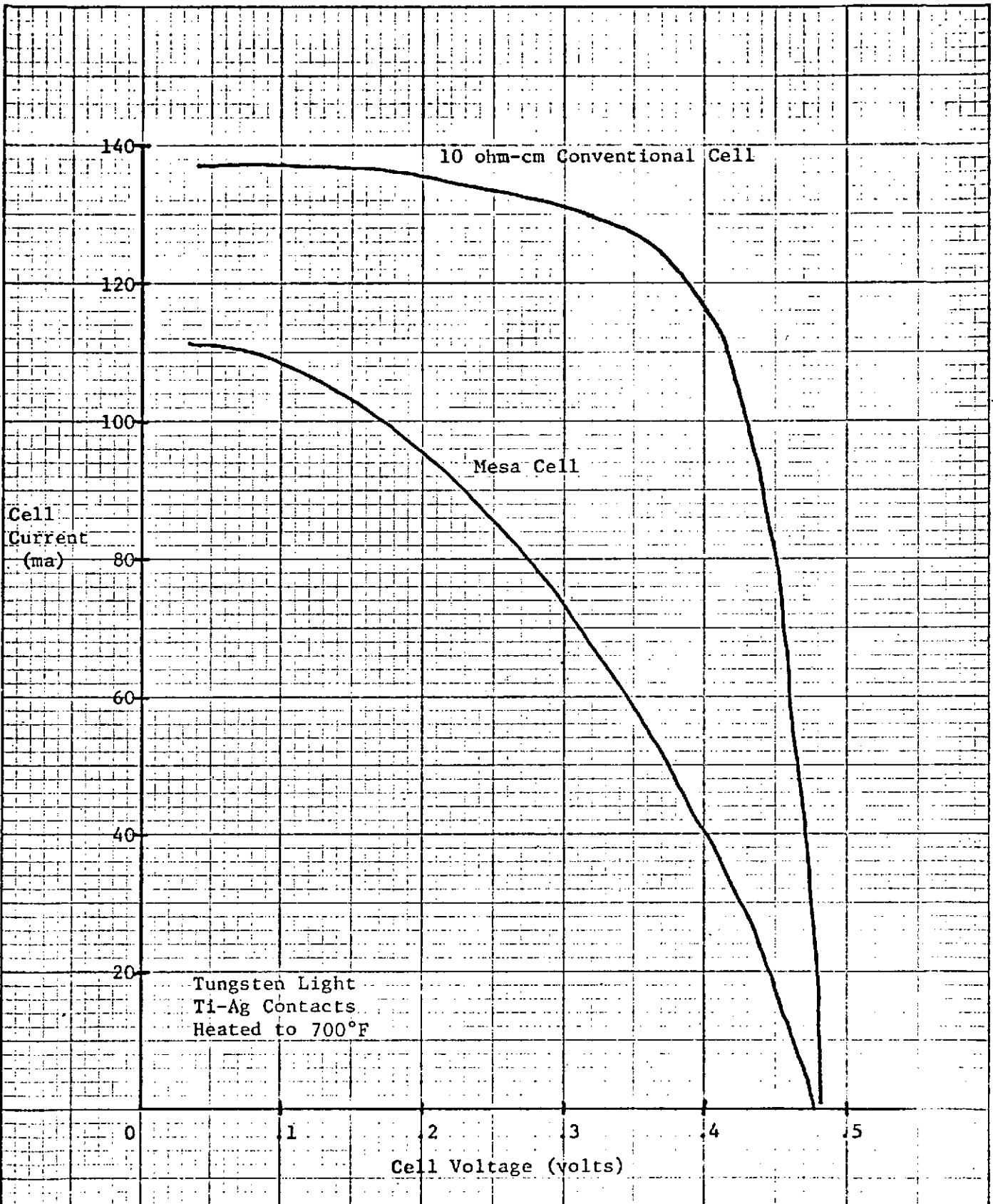


Fig. 11 Mesa Cell Output Compared to Conventional Cell

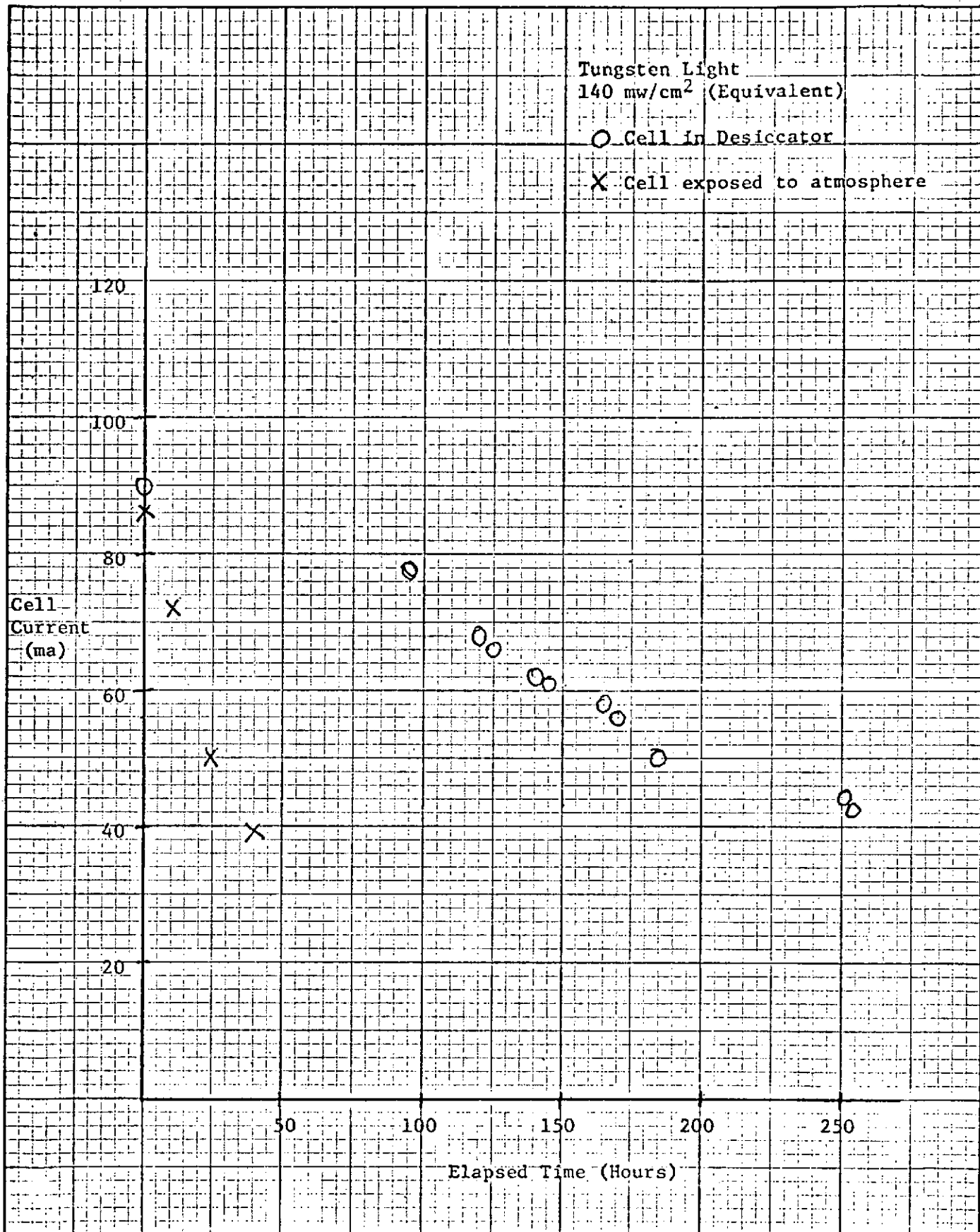


Fig. 12 Comparison of Output Decay of Mesa Cell in and out of a Desiccator

10... THE L... H...
7 X 10 INCHES
KE... G ES...

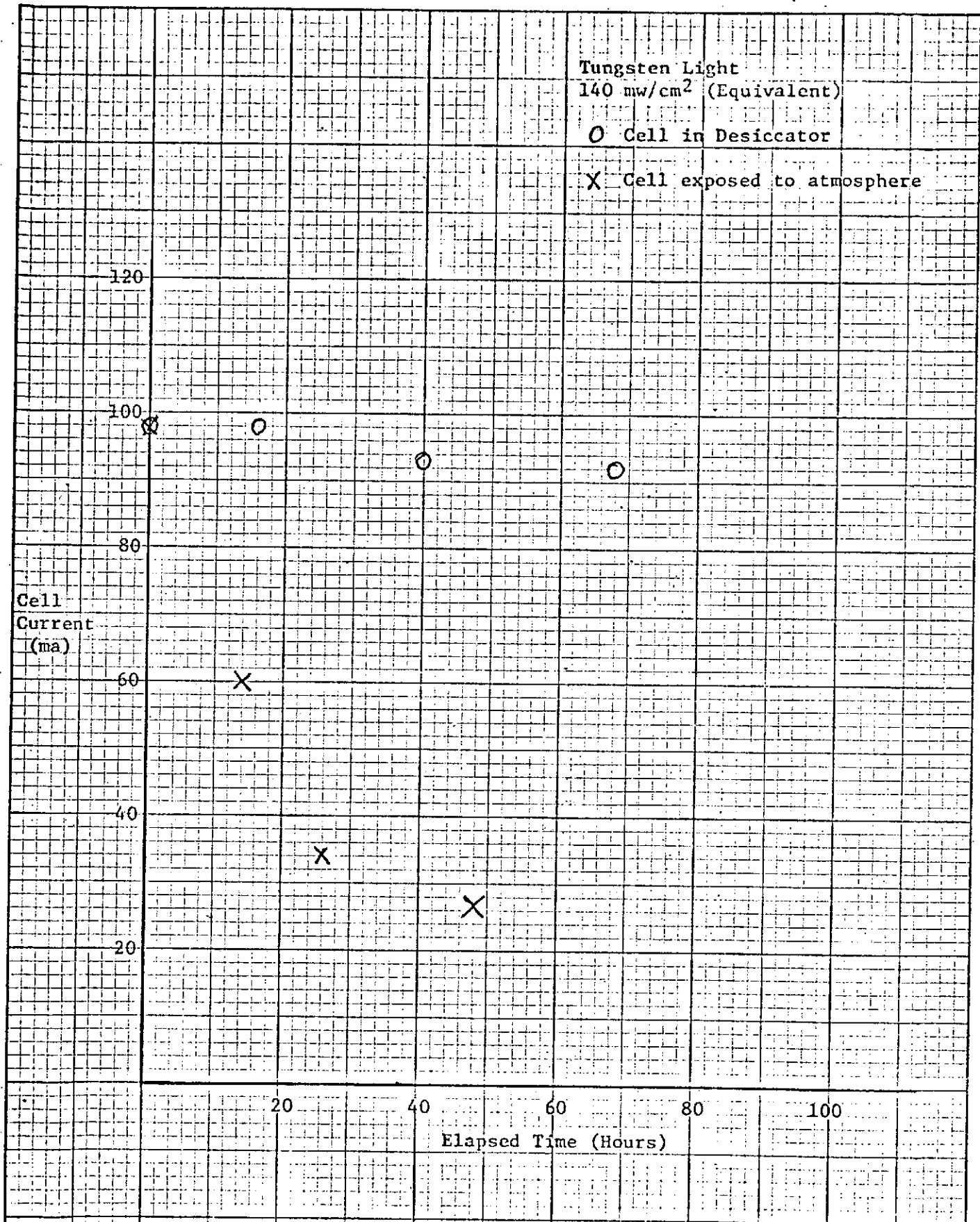


Fig. 13 Comparison of Output Decay of Mesa Cell in and out of a Desiccator

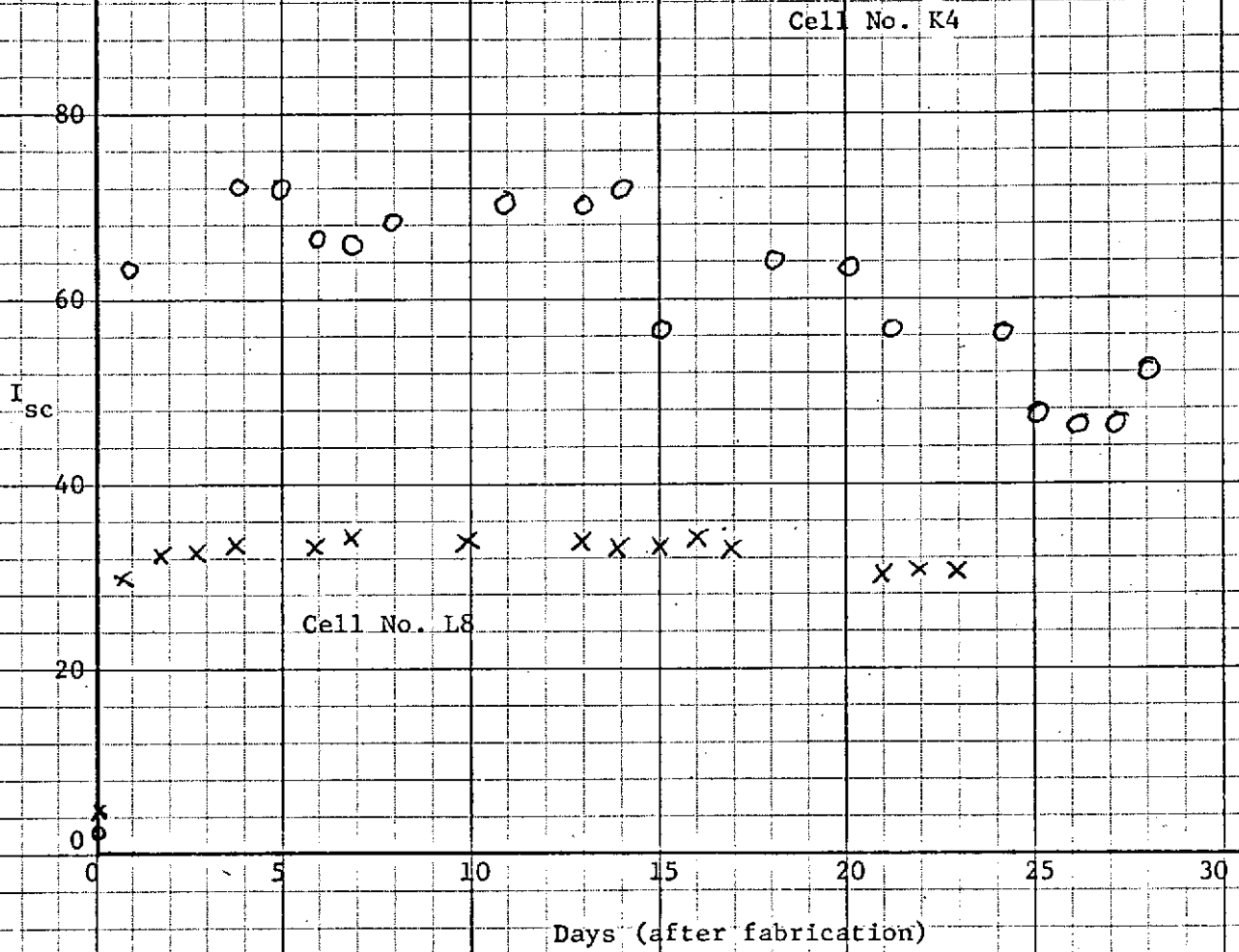


Fig. 14 I_{sc} vs. Days After Fabrication for the Tin Chloride Spin On Inversion Cells

Tungsten Source
140 mw/cm² (Equivalent)
Room Temperature

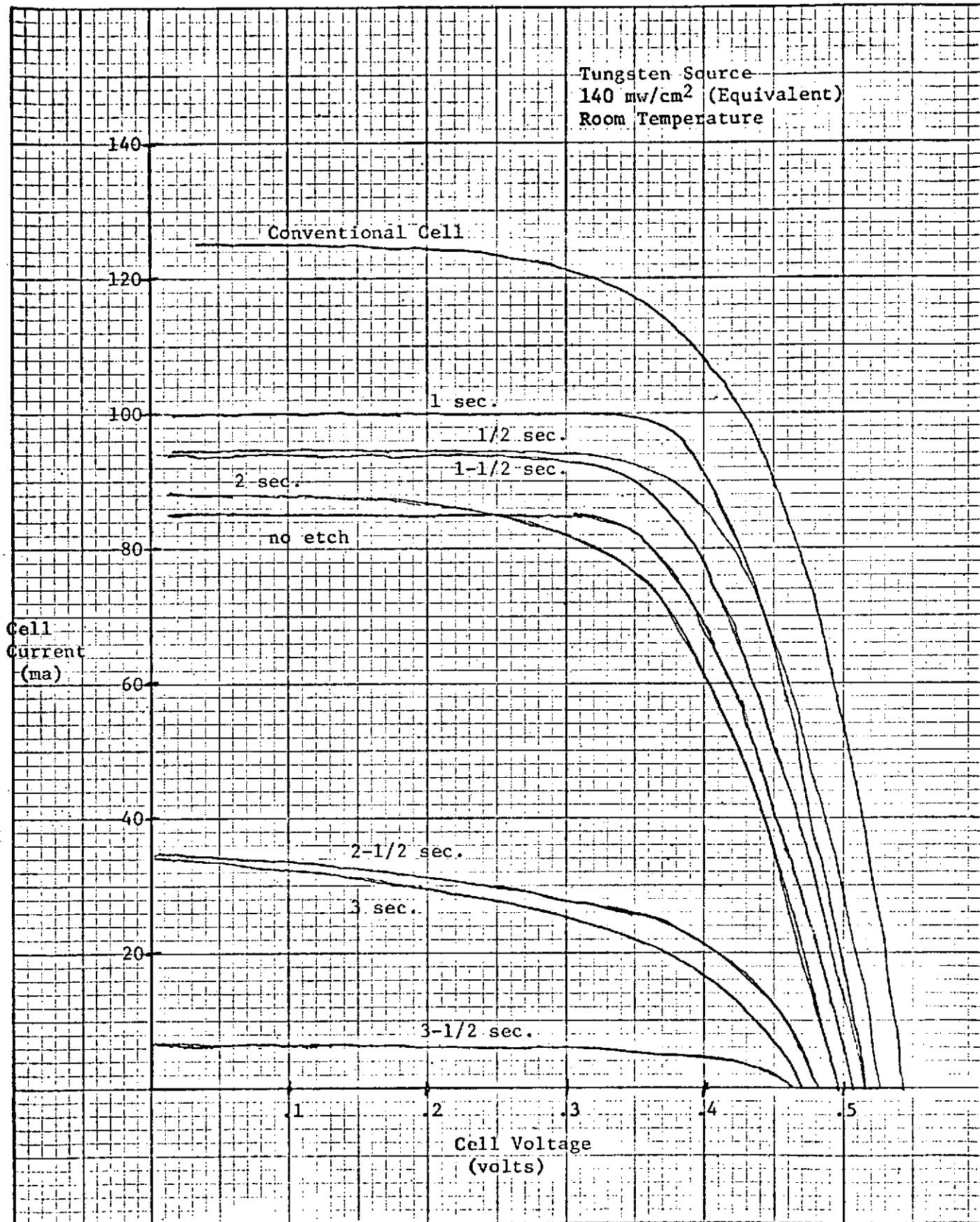


Fig.15 Comparison of I-V Curves for 8 Mesa Cells Etched for Different Times

10 X 10 T THE INCH 48 0/80
NEUFEL & ESSER CO.

10 X 10 TO THE INCH 45 0780
KEUFFEL & ESSER CO.

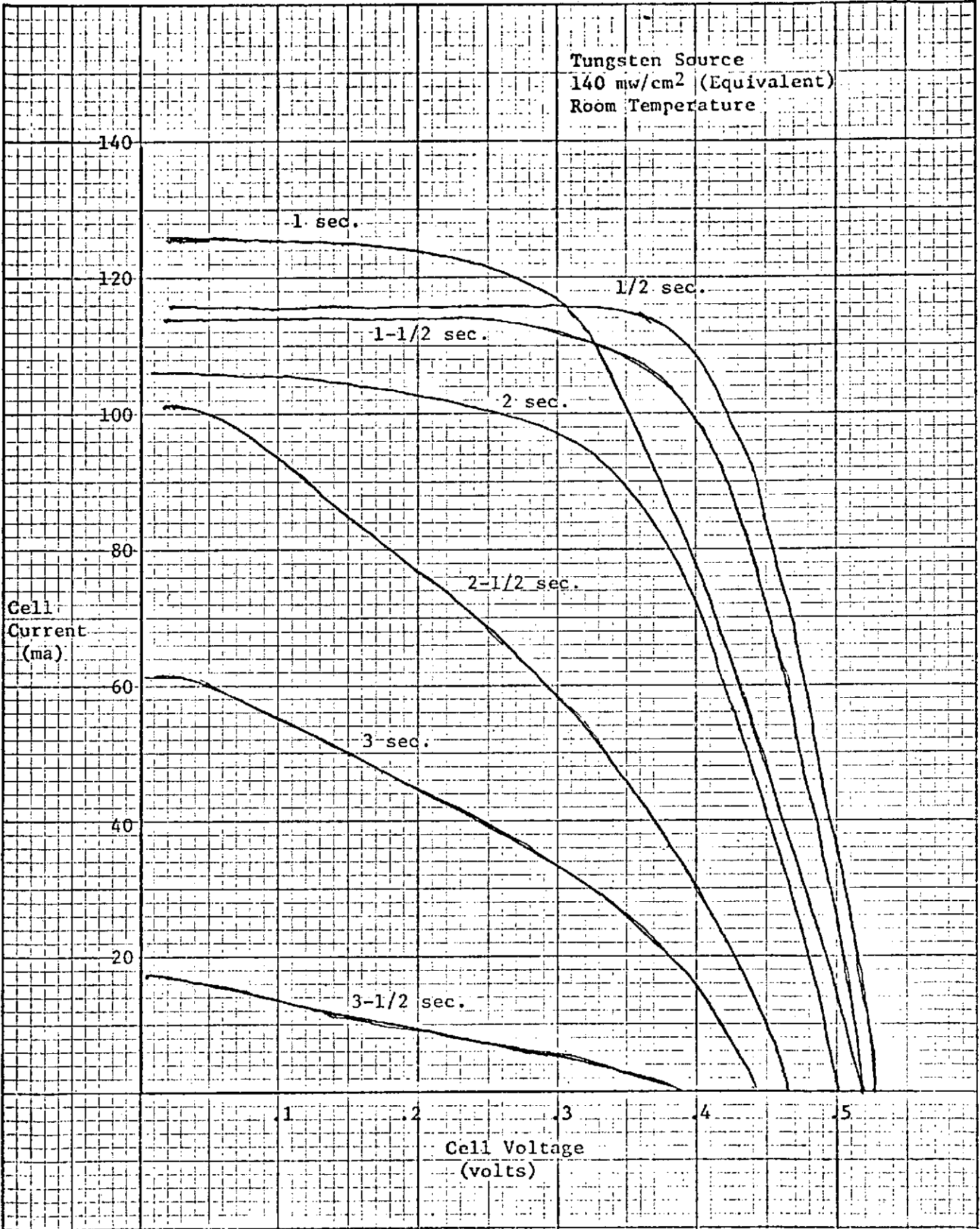


Fig. 16 Comparison of 8 Mesa Cells Etched for Different Times After a Sodium Silicate Application

Tungsten Source
140 mw/cm² (Equivalent)
Room Temperature

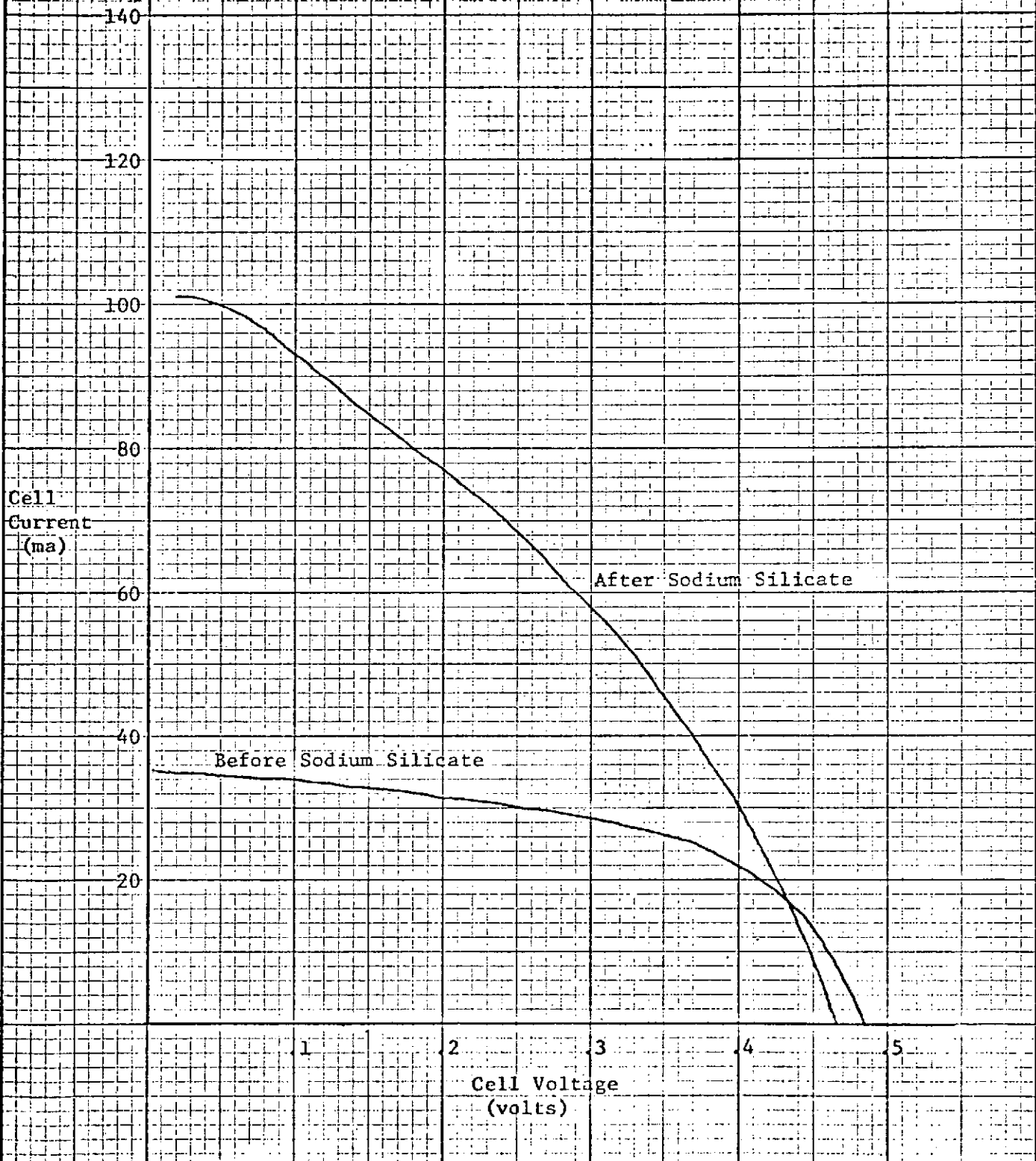


Fig. 17 Comparison of I-V Curves for 2-1/2 sec. Etch Cell Before and After Application of Sodium Silicate

3 INC
KEUFEL-ESSER CO.

Tungsten Source
 140 mw/cm² (Equivalent)
 Room Temperature

Cell Current (ma)

120

100

80

60

40

20

After 700°F Heat

After Sodium Silicate

Before Sodium Silicate

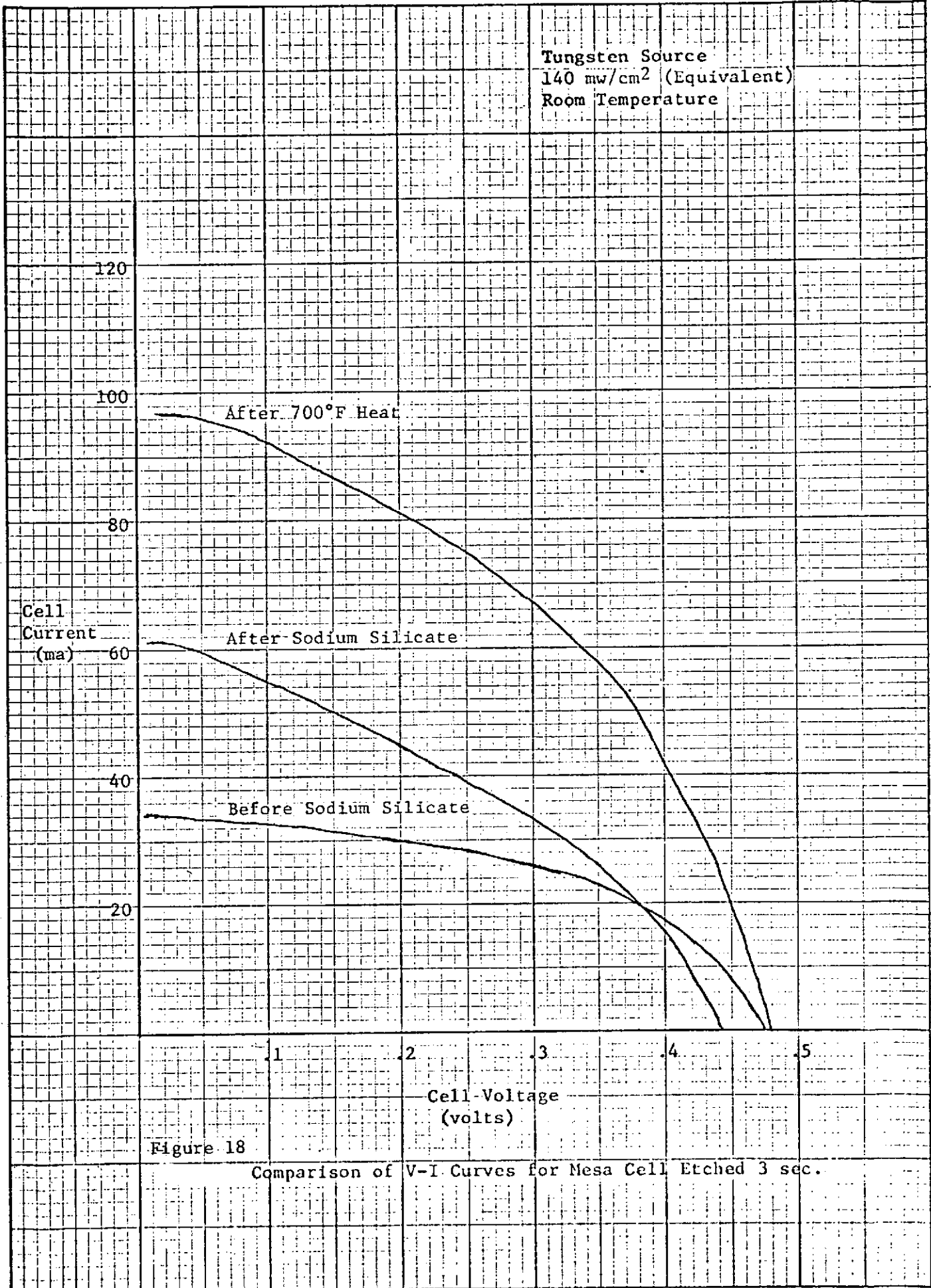
.1 .2 .3 .4 .5

Cell-Voltage (volts)

Figure 18

Comparison of V-I Curves for Mesa Cell Etched 3 sec.

10 X 10 TO THE INCH 46 0780
 KEUFFEL & ESSER CO.



Tungsten Source
 140 mw/cm² (Equivalent)
 Room Temperature

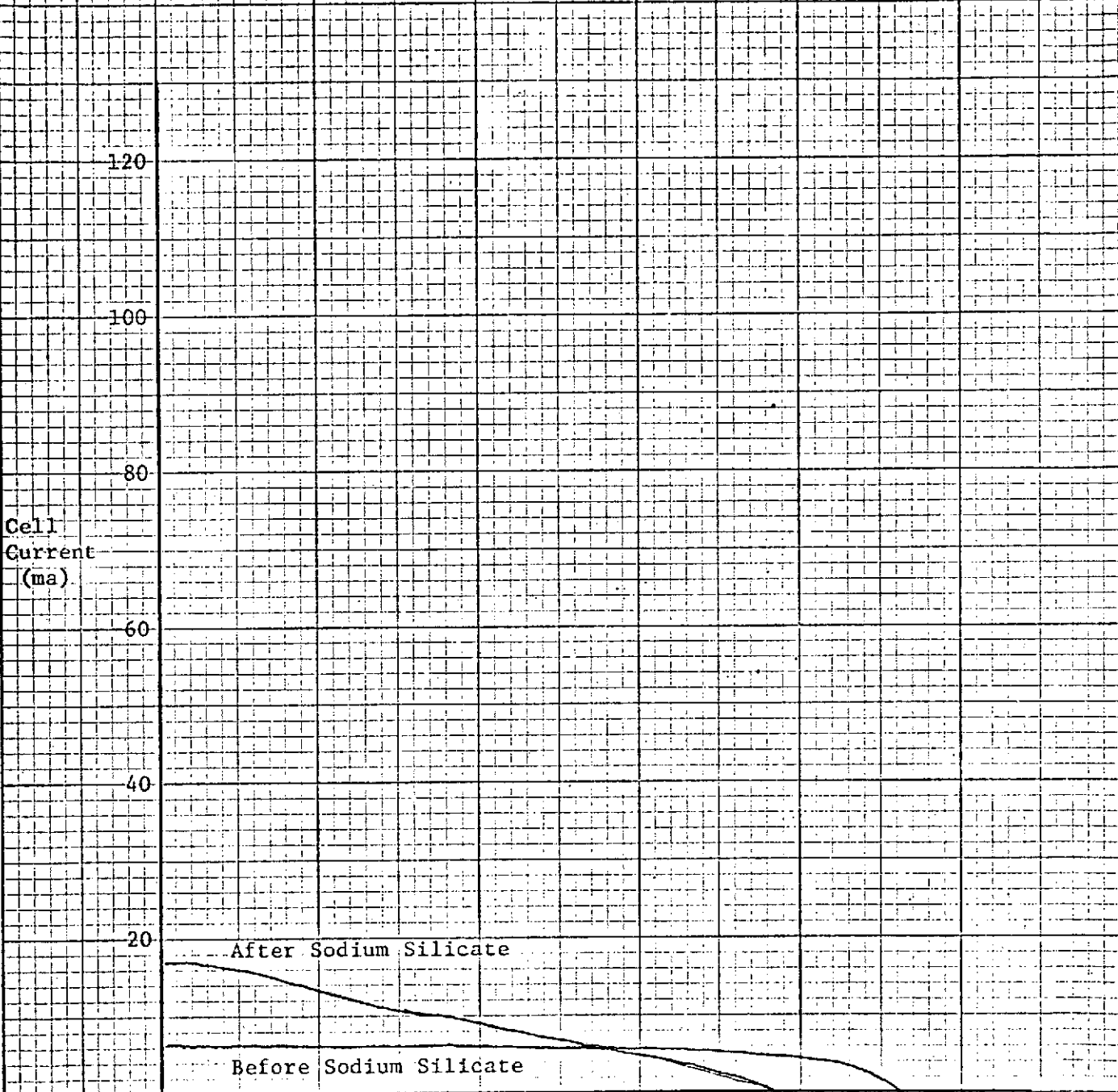


Figure 19

Comparison of V-I Curves for Mesa Cell Etched 3-1/2 sec.

10 X 10 TO THE INCH 46 0780
 KUFFEL & LESSER CO. U.S.

10 X 10 TO THE INCH 46 0780
7
KEUFFEL & ESSER CO.

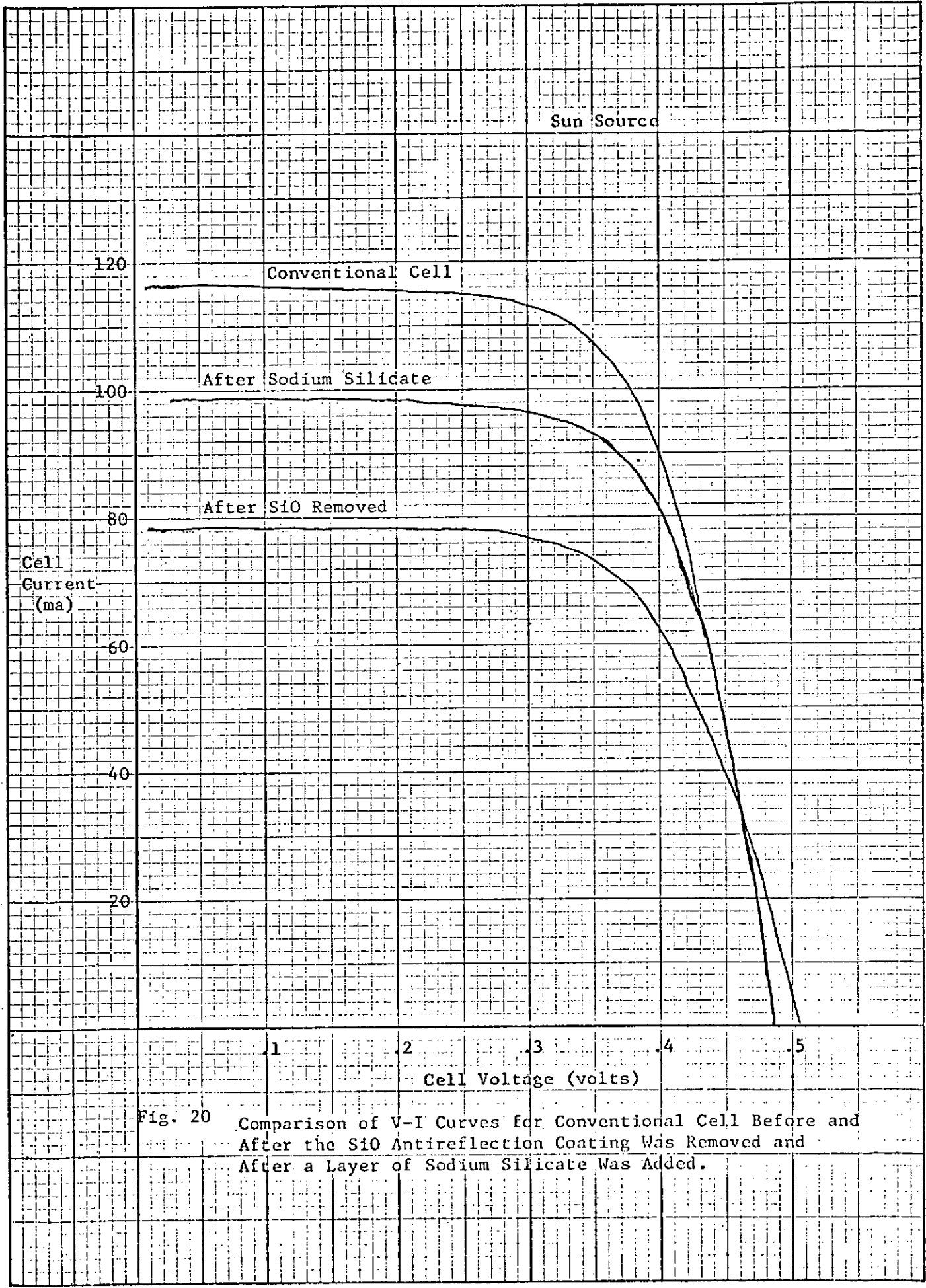


Fig. 20 Comparison of V-I Curves for Conventional Cell Before and After the SiO Antireflection Coating Was Removed and After a Layer of Sodium Silicate Was Added.

Comparison of a Contaminated Oxide Cell with a Conventional Cell.
Artificial Light Incandescent
140 mw/cm²

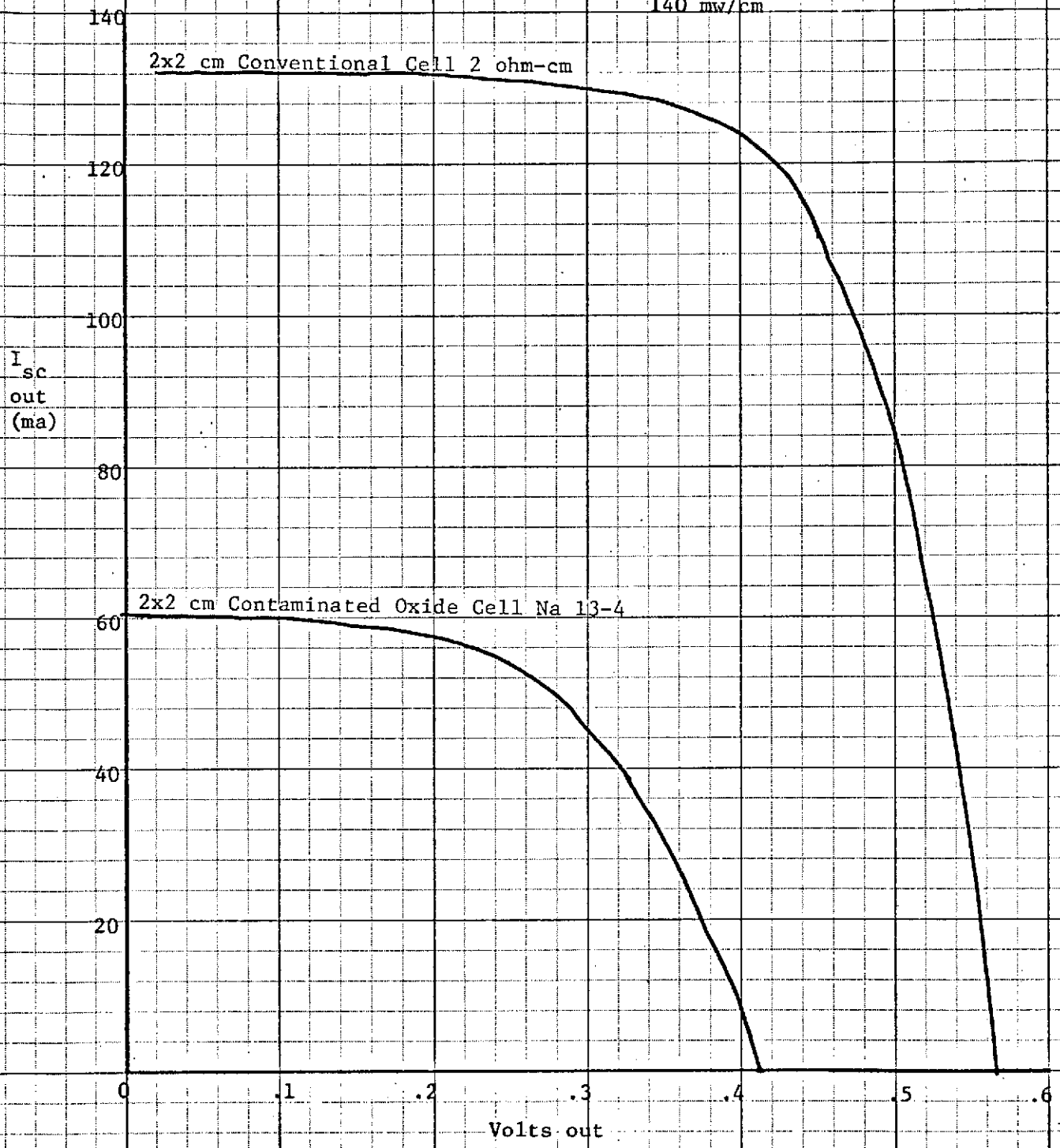


Figure 21

Comparison of a Contaminated Oxide Cell with a Conventional Cell.
Data taken in sunlight and adjusted for 140 mw/cm²

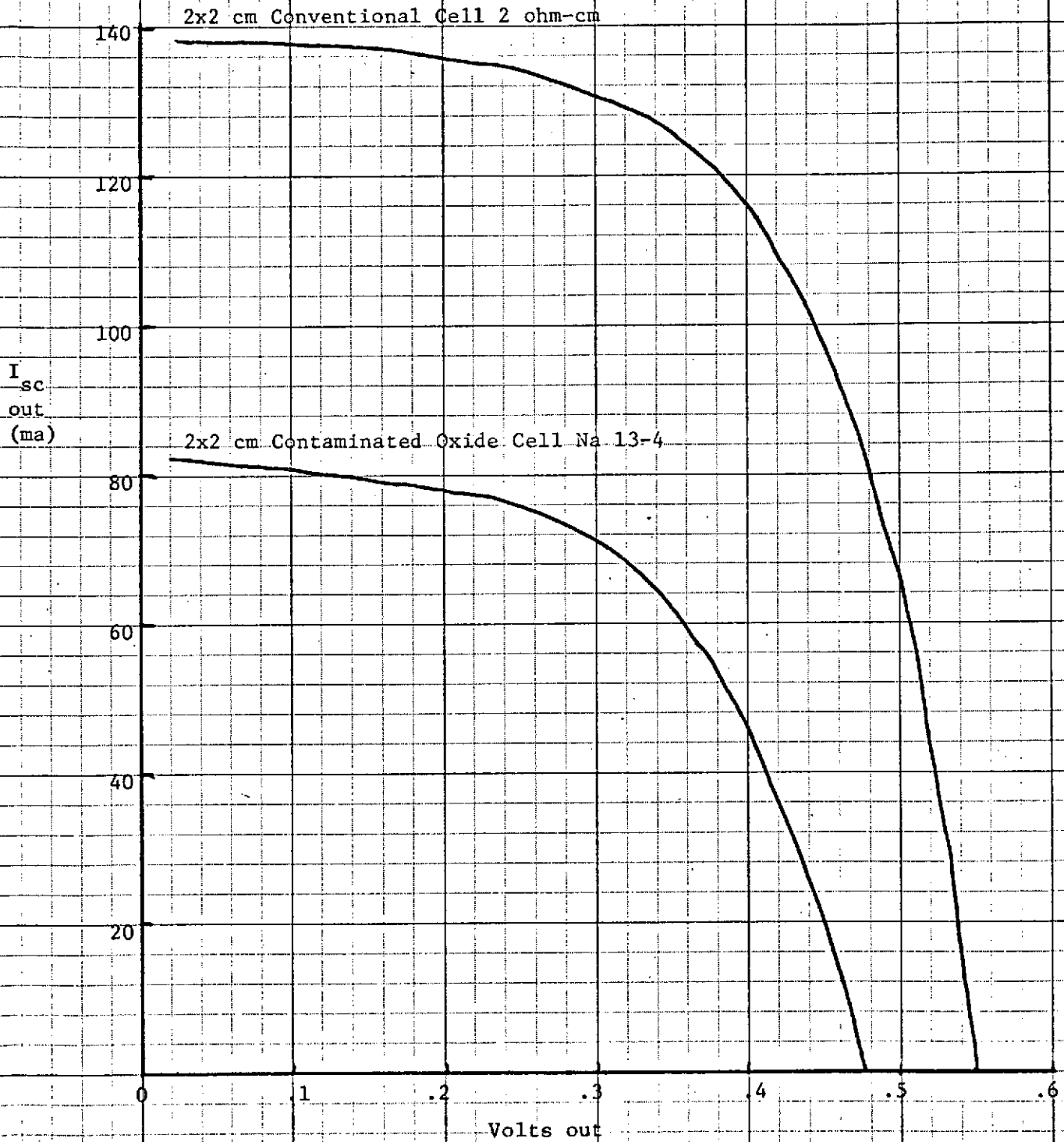


Figure 22

Curves taken in the sun
(118 mw/cm²)
2x2 cm wafers
30 finger contact pattern
Cell #Na 29-3

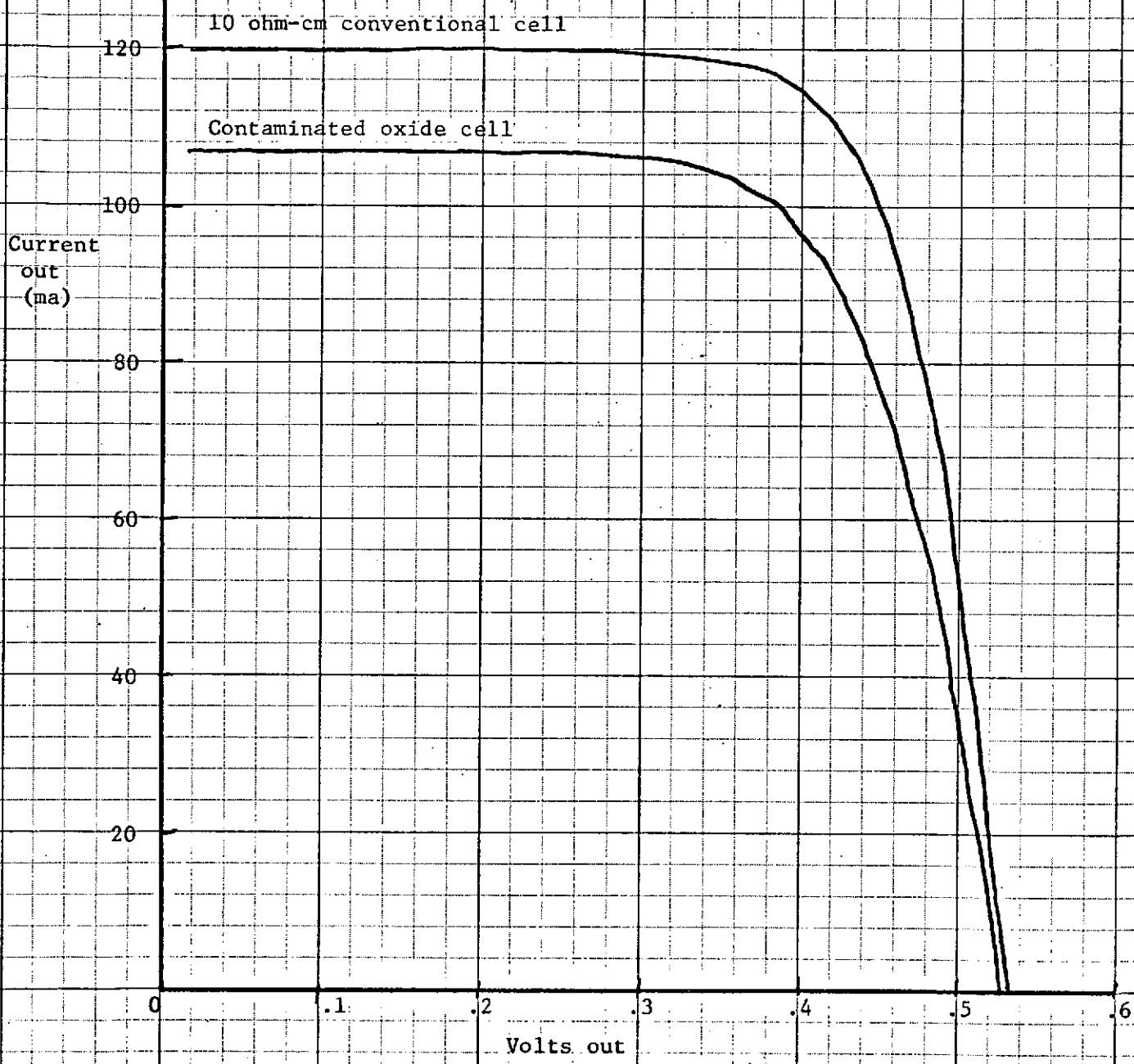


Fig. 23 Comparison Between Annealed Contaminated Oxide Cell and Conventional Cell

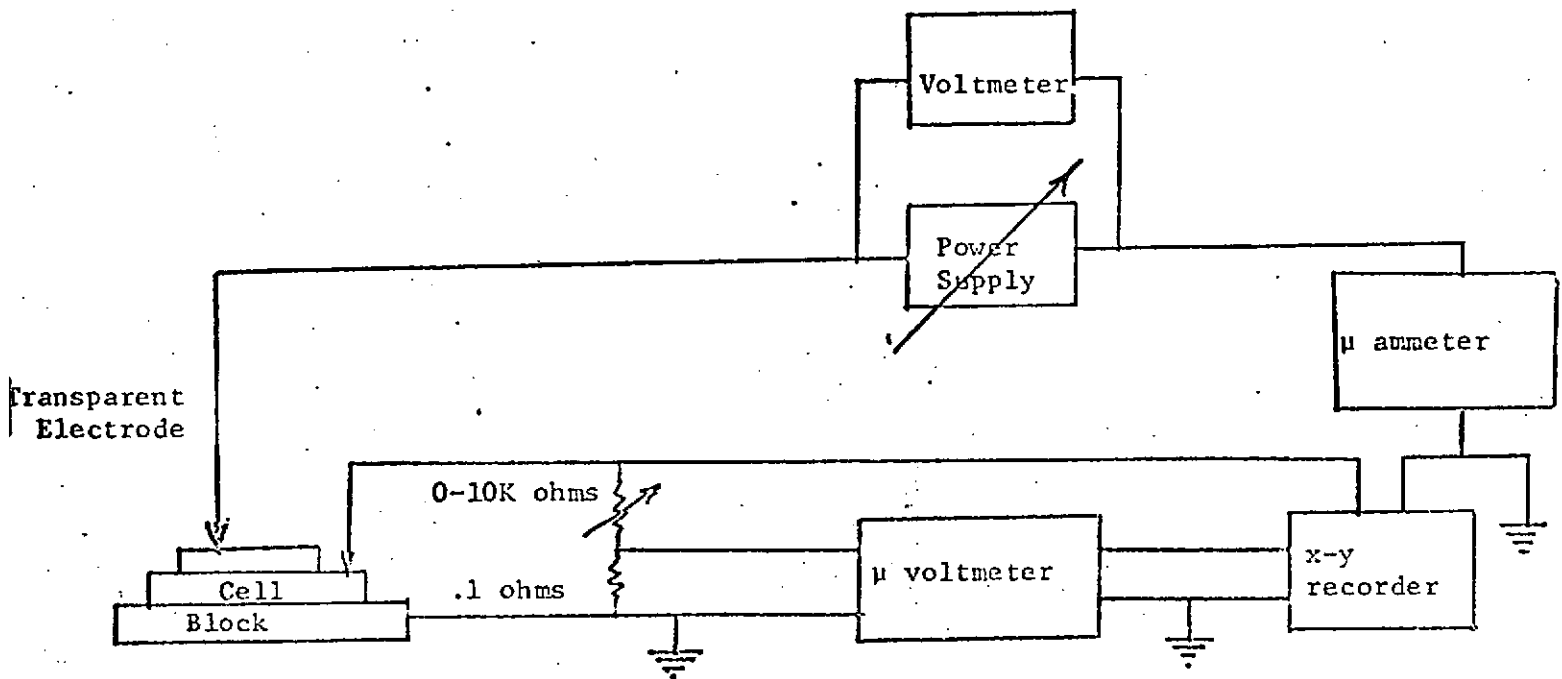


Fig. 24 Block Diagram of I-V Plotter