Photoelectric Properties of Ionically Bombarded Silicon

By EDWIN F. KINGSBURY and RUSSELL S. OHL

(Manuscript received March 25, 1952)

In the course of investigation of the rectifying properties of silicon very interesting photoelectric properties were found. The first photo-cells were cut from bulk silicon in which a natural potential barrier was found. A typical spectral characteristic of such a cell is shown. This early work was followed by the discovery of the ionic bombardment method of producing photo active silicon surfaces. The effects of the temperature of the target and of the energy of the bombarding particles in the photoelectric properties is illustrated by characteristic curves. Relative equi-energy spectral response characteristics as a function of wavelength are illustrated. The photon efficiency as a function of wavelength of a typical cell is shown.

INTRODUCTION

Because of the importance that barriers have come to assume in the general field of semiconductors the authors have been urged to publish results of their early experiments in this field. These experiments were undertaken in the course of a search for semiconductive material suitable for use as point contact rectifiers.

Before March 1941[1] one of the writers discovered a well-defined barrier having a high degree of photovoltaic response. The barrier was found only in melts of some lots of commercially available high-purity silicon. This barrier showed a high photovoltaic sensitivity to radiation from incandescent lamps.

The existence of this natural barrier was first observed in rods cut from melts for resistivity measurements. These rods showed a high degree of photovoltaic response, were found to have a high thermoelectric coefficient, and had good rectifying properties.[1] The fact that one end of the rod developed a negative potential when illuminated or heated and that when supplied with a negative potential showed low resistance to current flow across the barrier led to the terminology of *n*-type silicon. The material of opposite type was named *p*-type. Material of the *n*-type is now known to derive its electrical properties from the presence in the crystal lattice of electron donor impurities, for example phosphorus, while *p*-type derives its electrical properties from the presence of electron acceptor impurities, such as boron. In this paper some of the results of investigations of the natural barrier are reported; however, the photovoltaic properties of induced barriers obtained by the ionic bombardment of *p*-type silicon will be given more detail treatment.

EARLY RESULTS

The approximate location of the natural barrier found in early melts is shown in Fig. 1. The barrier was generally located in the melt perpendicular to the axis of the melting crucible or more accurately to the direction of the temperature gradient. Plates and rods containing sections of the photoactive barrier, Fig. 1a, were cut from the melt and mounted on convenient supports for laboratory tests. Fig. 1c shows a magnified section of one of these barriers.[2]

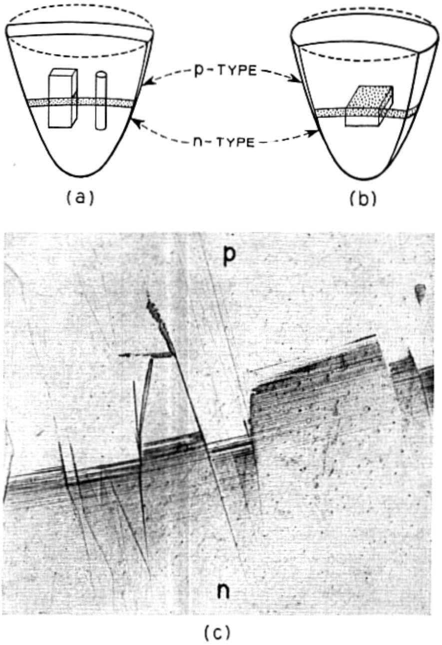
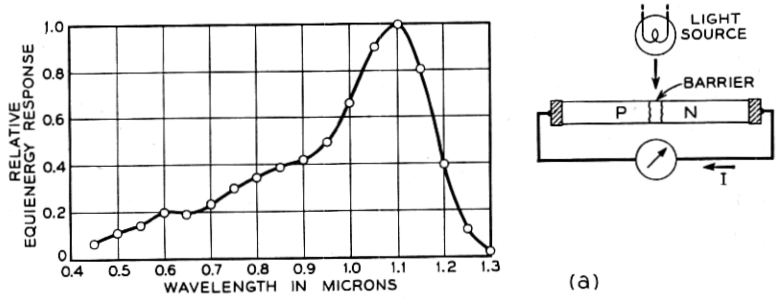
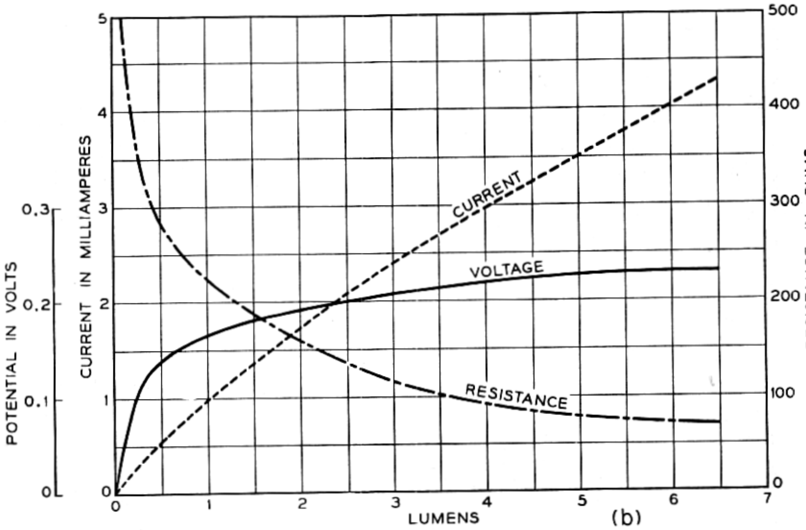


Fig. 1—(a) Drawing of melt showing position of photovoltaic barrier and photo cells with natural barrier. (b) Drawing of melt showing surface type photo cell made from natural barrier. (c) Magnified, etched section of slowly cooled silicon showing the transition between p and n silicon forming the barrier which consists of intermeshed striae of these two varieties.





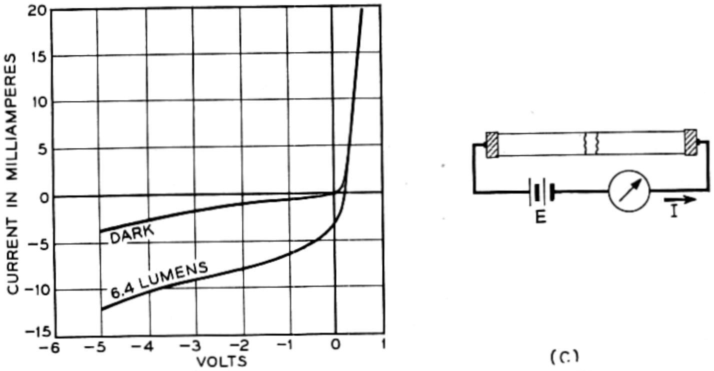


Fig. 2a—Spectral response of internal barrier in silicon.
Fig. 2b—Voltage and current photosensitivity of internal barrier in silicon.
Fig. 2c—Rectification characteristic of internal barrier, dark and illuminated.

A typical spectral response curve of such a barrier is shown in Fig. 2a while Fig. 2b gives its open circuit voltage, short-circuit current and resistance when illuminated by a tunsten light of 2848°K color temperature. This cell resistance was taken as equal to that of an added series resistance which reduced the short-circuit photocurrent to one-half. The value so obtained is somewhat higher than the corresponding ratio of the voltage and current given in the figure. Fig. 2c gives the behavior as a rectifier in the dark and with a stated light on the barrier.

Cells whose barrier was near the surface were made by cutting close to the natural one as shown in Fig. 1b. This cut exposed large photoactive areas. Surface barrier activity was occasionally found on the top surface of some melts. These surface type cells showed a wider spectral response toward the visible than the internal barrier type. This was found to be due to the spectral absorption characteristics of the bulk silicon. A further discussion of this appears later in the paper.

These early barrier cells showed remarkable stability under severe temperature conditions. For instance, they could be heated to redness in air and quenched in water with no serious change in their characteristics. They were tested in liquid nitrogen, under water and in oil without injury. They could be illuminated with direct sunlight with no injury to their response characteristics other than the temporary effect of the increased temperature. Several of these internal barrier cells have been in use in test circuits for more than ten years with no serious change in their photoresponse properties. These observations seemed to indicate clearly that a very high degree of stability could be expected from silicon photocells.

However, there were serious practical disadvantages to the early cells. Those shown in Fig. 1a were active near the exposed barrier itself which was usually a strip along the surface about ½ mm wide. On the other hand, the surface types as shown in Fig. 1b showed irregular responsiveness over the surface area.

From these early studies it was clear that if a good method could be found to activate large areas of silicon surfaces uniformly, cells could be made which might compete with other kinds of surface barrier type cells already available. The search for such a process resulted in the ionic bombardment method of activating silicon surfaces. Such surfaces also have desirable rectifying properties.[3]

METHOD OF PREPARATION

Hyper-purity silicon was used for bombardment type cells to avoid the formation of natural barriers due to minute impurities and to give better control of the sensitivity. After being cast in a fused silica crucible, the roughly cylindrical piece was ground to a cylinder about 1½″ diameter, a process which removed crucible contamination and gave a convenient size for slicing into wafers about 0.025″ thick. The two faces were then made approximately flat and parallel after which one was left rough and the other ground and polished down to a good optical surface. In most cases the discs were then cleaned by soaking for approximately fifteen minutes in a solution of hydrofluoric acid, rinsed in distilled water and dried.

The activation consisted of exposing the polished face to a uniform beam of positive ions of helium at a pressure of 10^{-3} to 10^{-4} mm of mercury. The energy of the particles used in different units ranged from 100 to 30,000 electron volts. During this bombardment the silicon surface was kept at a favorable temperature, about 395°C.

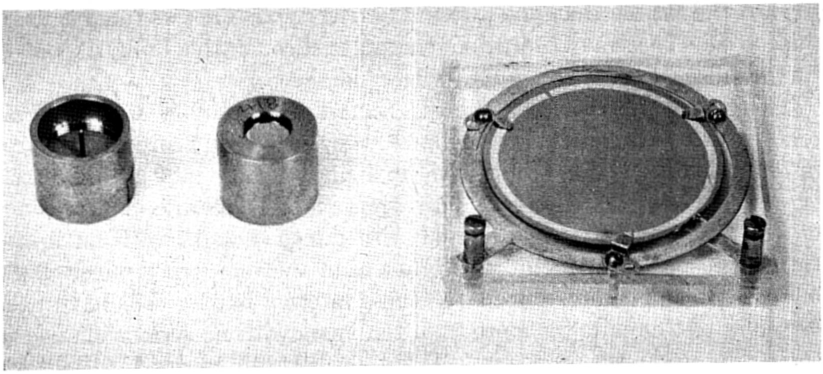


Fig. 3—Intermediate and large size photocells made by ion bombardment. Back of the intermediate also shown.

After activation, collector electrodes of evaporated rhodium were applied. Cells of three sizes have been constructed, two of which are shown in Fig. 3, the intermediate and the large one, of exposed active areas about 0.40 and 8.0 sq. cm. respectively. A small one had an area around 0.005 sq. cm. Most of the measurements reported in this paper have been made with the intermediate size.

EFFECT OF ION VELOCITY

That ion velocity has a profound effect on the voltage current characteristic of bombarded surfaces is shown in Fig. 5. These characteristics were obtained by placing a tungsten point contact under 10 gm of force,

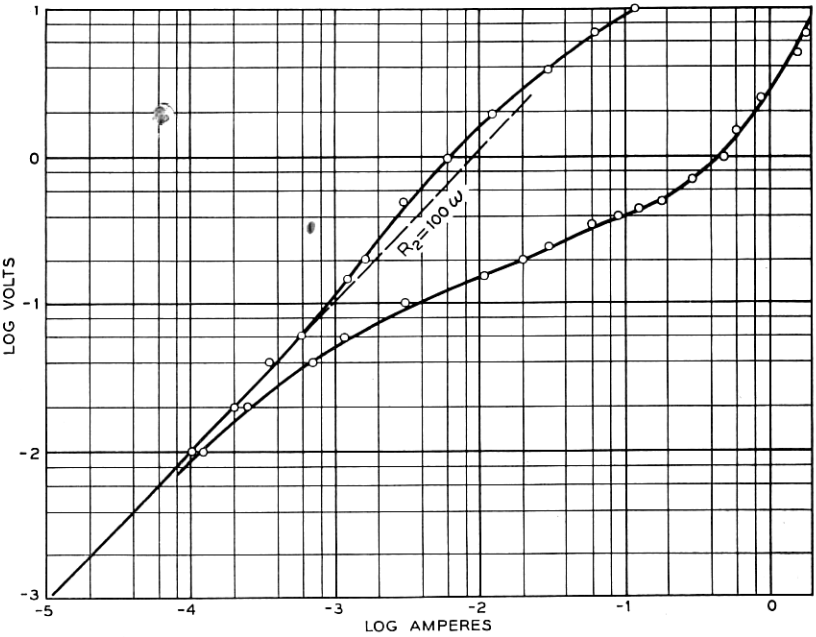


Fig. 4—Rectification characteristic of the large photocell.

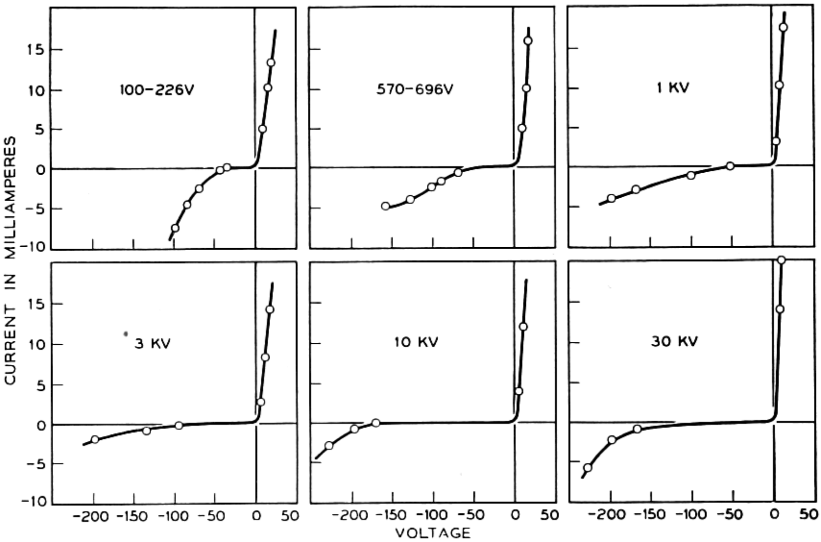


Fig. 5—Effect of bombardment voltage on the rectification of the intermediate cells.

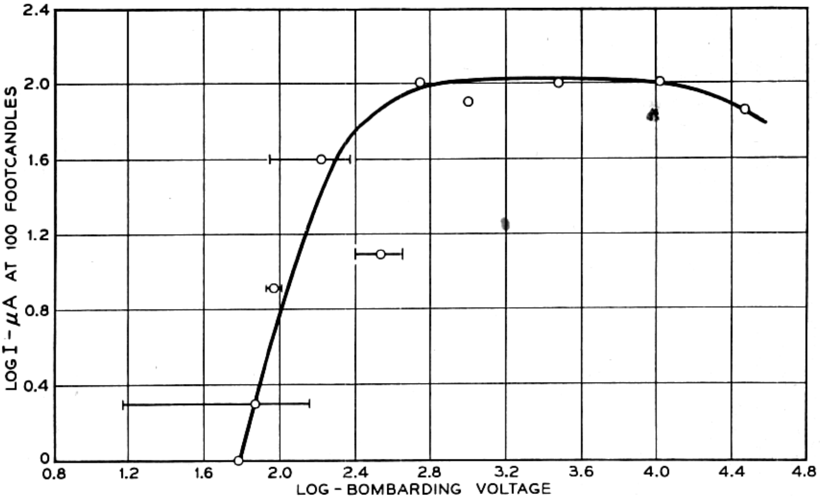


Fig. 6—Photocurrent at a constant illuminance versus the bombarding voltage.

on the photo active surfaces of the medium size cells whose spectral response is given in Fig. 8. However, in order to show the rectifying property of the barrier without the complication of a point contact, a disc of hyper-purity silicon $1\frac{1}{2}''$ in diameter and about $0.025''$ thick was given an optical polish on both faces. One face was bombarded with 30-kv ions.

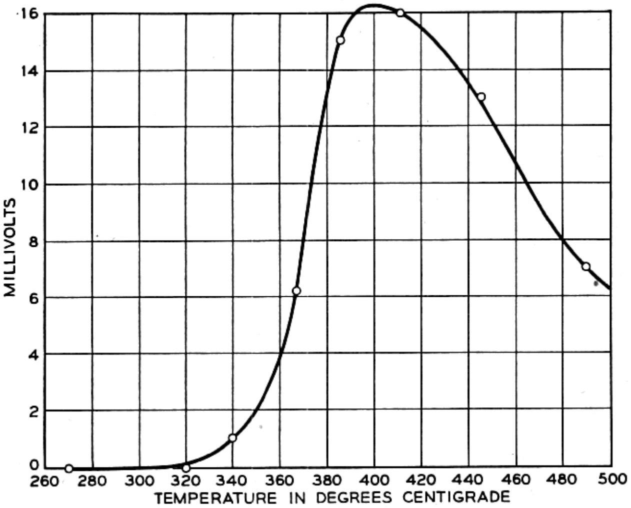


Fig. 7—Photovoltage at a constant illumination versus temperature of the bombarded silicon surface.

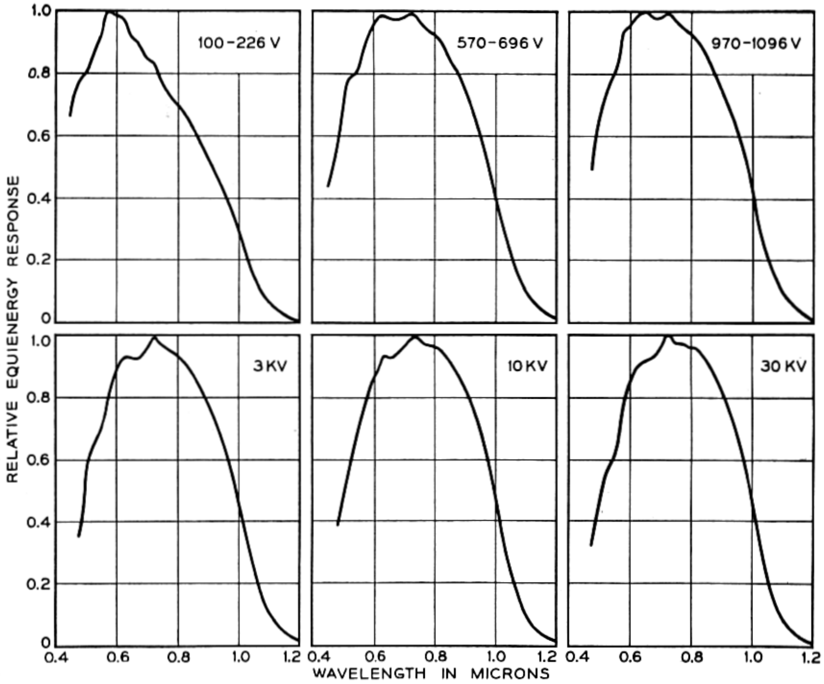


Fig. 8—Spectral response of the intermediate size cells at various bombarding voltages.

Electrodes $1\frac{1}{8}''$ in diameter of evaporated rhodium metal were applied in like manner to each surface. Contact was made to the collector electrodes by means of tin discs. Fig. 4 gives the forward and backward log voltage-log current relation of this large cell. Without bombardment such an arrangement shows ohmic conductivity so it is evident that the treatment is responsible for the development of a potential barrier beneath the surface. It is believed from the high dark resistivity of the bombarded layer that the intrinsic properties of the silicon are developed therein. Thus an intrinsic -*p* type potential barrier is produced similar to a degree to the *n*-*p* junction. One would expect the depth of this barrier to be related to the velocity of the ions. Consequently a study has been made of the effect of ion velocity on the photoelectric properties.

The photoelectric current at constant illuminance for a series of cells prepared by bombardment with ions of different energies is shown in Fig. 6. It is remarkable how quickly and completely the current sensitivity saturates at approximately 500 volts.

EFFECT OF SURFACE TEMPERATURE DURING BOMBARDMENT

In the preparation of photocells it was found that the surface temperature during bombardment had a pronounced effect on the efficiency. In order to study this effect it was necessary to determine the surface temperature of the silicon itself. Since it was impractical to measure the silicon temperature during bombardment, a calibration was made of the surface temperature in terms of the temperature of the graphite heating block. This calibration was carried out by two platinum/platinum rhodium thermocouples made of 5-mil wires. The fused thermojunction beads were held in contact with the surfaces by miniature tungsten springs. Temperature measurements with the thermojunction in contact with the silicon surface were subject to error from the slightest contamination at the point of contact. Perhaps the most difficulty was due to a reaction between the platinum and silicon at temperatures above 400°C.

The effect of surface temperature on the photoresponse is shown in Fig. 7. It is apparent that maximum sensitivity results when the target is kept at about 395°C. Perhaps by coincidence this is also the temperature at which no Hall Effect is observable in this hyper-pure material.

Cells prepared at temperatures above the critical value show lower back resistances than those prepared at the critical temperature and conversely those at temperatures below the critical value have higher back resistances but a much reduced photoresponse.

EFFECT OF TOTAL BOMBARDING CHARGE

The photoresponsiveness improves as the total bombarding charge is increased until it has reached about 600 microcoulombs per sq. cm. Further bombardment produces no appreciable improvement. In certain exploratory tests a total charge of about 9000 microcoulombs at 30 kv has been applied. Under these severe conditions the surface may show small areas having a slightly etched appearance.

No extensive tests have been made to determine the effect of the rate of application of the bombarding charge. The apparatus was designed for use at a rate of about 5 microamperes per sq. cm. It is known however, that between the limits of about 2.5 and 10 microamperes per sq. cm. the effects are subject only to the total charge or the total number of ions which strike the silicon surface.

EFFECT OF BOMBARDMENT VOLTAGE IN SPECTRAL RESPONSE

Six spectral curves are shown in Fig. 8 which illustrate the result obtained with the intermediate size cells over the bombardment voltage range previously mentioned. The peak of the lowest voltage cell is definitely toward the blue compared with the other five whose maximum is constant at about 0.725 μ.

One objective in this study was to obtain evidence relating to the depth of the barrier below the silicon surface as a function of the energy of the bombarding particles. The higher the velocity of the particles the further beneath the surface one would expect the barrier to be located and as a result there might be a shift in the spectral characteristic toward the red with increasing depth of the barrier due to the relatively greater absorption at the blue end. There is however, a selective or secondary maximum at the peak which sharpens it and nullifies the effect of the warping of the entire curve. The blue to red shift can be shown as in Fig. 9 by plotting the ratio of the responses in Fig. 8 at 0.50 μ and 1.0 μ. Thus at low voltage the blue to red ratio is high and decreases as the bombarding potential is raised.

In the spectral curves it will be noted that there are a number of secondary humps located near the top of the curves and extending down on the blue side. There is a strong tendency for them to occur at definite wavelengths and to be evenly spaced regardless of the bombarding voltage.

SPECTRAL MEASUREMENTS ON THE LARGE CELLS AND THE EFFECT OF MATERIAL COMPOSITION

For the large cells, two grades of silicon were used both prepared by pyrolytic reduction of $SiCl_4$ and called "hyper-pure". These will be

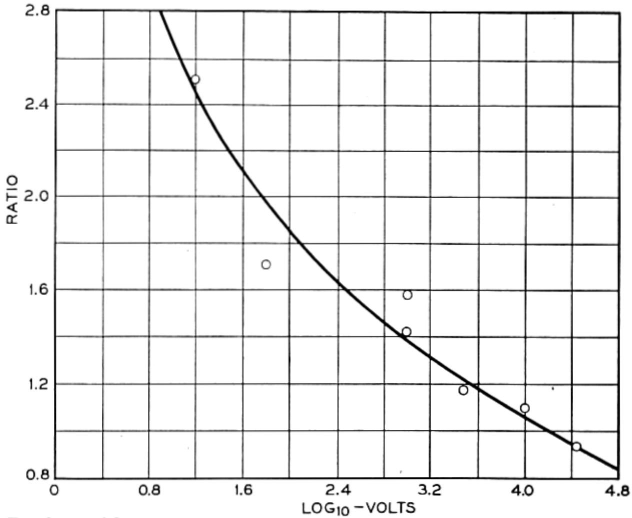


Fig. 9—Ratio of blue to near infra-red response versus bombarding voltage.

designated B and C, the former being from the same source as "silicon B" referred to in the paper by Scaff et al.[2] A typical analysis is given therein. The C silicon was from another source and a spectroscopic analysis indicated it was somewhat more impure than B thus agreeing with observed differences in its electrical and optical characteristics. An optical variation of considerable interest is shown in Fig. 10 where the spectral transmittance of the two grades of silicon is compared in the infra-red for polished plates each 0.0195″ thick.

The transmittance of B decreases a little with increasing wavelength but C goes down much more. Both however, start to get transparent at about the same point, 1.1 μ and also show corresponding absorption bands superimposed on the main curve. Briggs[4] has compared the transmittance from 2 μ to 12 μ of the A and B silicons in Scaff's paper where the former was much more impure than the C grade. The absorption of the A silicon increased so rapidly out in the infra-red that a much thinner sample was used for the measurements than for the B material. If this difference in thickness is allowed for, the effect of impurity is very striking.

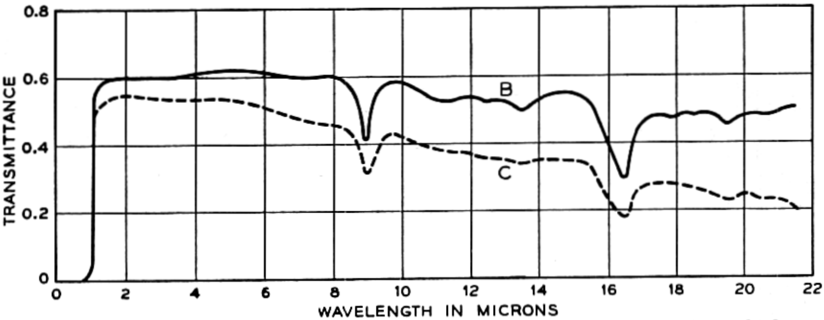


Fig. 10—Spectral transmittance of B and C grades of silicon, polished plates, 0.0195″ thick.

The spectral response of large area cells made of the B and C materials and bombarded with 1000-volt helium positive ions is shown in Fig. 11. The two curves are similar in shape except the one for C silicon is somewhat narrower and in addition is shifted toward the blue. Both have some of the secondary humps noted previously.

All the cells shown in this paper have indicated a long wave limit of about 1.2 μ. Actually some response can usually be detected out to about 1.3 μ. Measurements made some years ago on the internal barrier units also gave a limit around 1.3 μ but relatively more response at 1.2 μ with peaks close to 1.10 μ. This difference is reasonable because light was projected along the barrier plane and not normal to it as in the latest units, so that with the rapidly increasing transparency in this region, less infra-red radiation was lost. However, the blue was rapidly attenuated.

When illuminated by tungsten light of 2848°K color temperature, the large B cells gave 2160 microamps per lumen and the C unit 638. Correcting for a surface reflectance of 0.385, the net sensitivities would be 3510 and 1040. These measurements were made with between 4- and 5-footcandles illuminance on the cells, a region in which the response is proportional to the intensity. At much higher values of illuminance there was some falling off of response so that the effective sensitivity was a little lower. The above measurements were made on a ten ohm microammeter which is too low a resistance to affect the linearity. The intermediate cells ran approximately 3000 microamps per lumen in the most sensitive region of bombardment without correction for surface reflection and at 10- to 20-footcandles for the same tungsten lamp using a meter of 76 ohms.

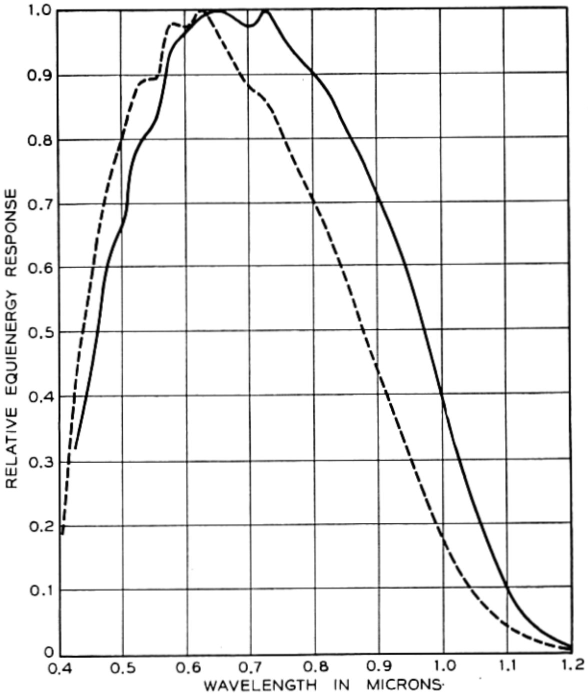


Fig. 11—Spectral response of large size photocells of B and C grades of silicon.

PHOTON EFFICIENCY

It is of interest to examine the spectral photon efficiency of a cell made by bombardment. As an example, there may be taken the 3-kv cell whose spectral response is shown in Fig. 8. When illuminated by a tungsten light of 2848°K color temperature at 10-foot candles, a sensitivity of 3090 microamps per lumen was secured. Allowing for a surface reflectance loss of 0.385, this value becomes 5020 for the radiation actually absorbed. From these data the sensitivity in microamps per microwatt at the peak 0.725 μ, calculates to be 0.388 and the photon efficiency, i.e., the electrons per photon, 0.66. Fig. 12 gives the efficiency through the spectrum. Note that the efficiency rises some on the short wave side shifting the peak of the equi-energy curve (Fig. 8) over to 0.625 μ. This increase is evident from the fact that if the equi-energy curve decreased linearly from the peak at 0.725 μ to zero at 0 μ, the photon efficiency would remain constant and equal to that at 0.725 μ. For the purpose of the above calculation, the curve in Fig. 8 has been taken as going to zero at about 0.40 μ, a fact experimentally checked. If unity is considered to be the maximum possible efficiency at any wavelength, 72 per cent of it is attained at 0.625 μ and nearly half of the spectral range is 50 per cent or higher.

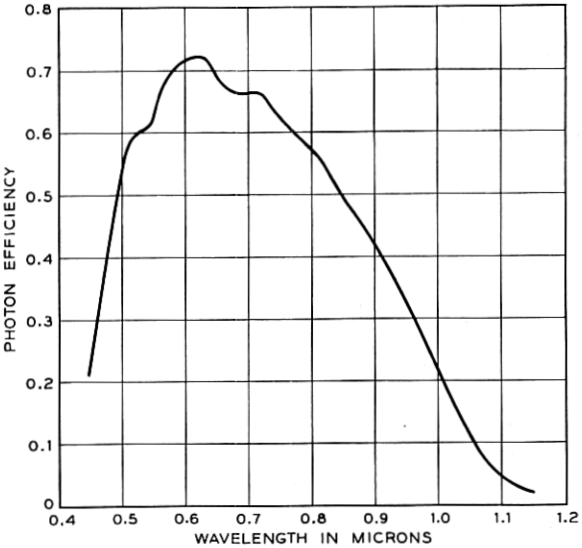


Fig. 12—Spectral photon efficiency of the 3-kv cell of Fig. 8.

CONCLUDING REMARKS

These experiments have served not only to introduce us to some of the phenomena involved in semiconductor barriers but have also yielded photo cells having desirable properties. These cells have a high degree of stability and will stand treatment ruinous to most other cells. They have a very high current sensitivity to tungsten light and daylight. They require no associated battery and can be made in large areas. Unlike the material used in many types of photo cells, silicon does not have the disadvantage of scarcity. All tests to date indicate that an indefinitely long life may be expected even under extreme illumination. Fig. 11 suggests that it may be possible to control to some extent the spectral response in the region from the deep blue into the infra-red. The long wave limit is set by the edge of the absorption characteristic.

REFERENCES

1. U. S. Patent No. 2,402,839, Filed Mar. 27, 1941.
   U. S. Patent No. 2,402,662, Filed May 27, 1941.
   U. S. Patent No. 2,443,542, Filed May 27, 1941.
2. J. H. Scaff, H. C. Theuerer and E. E. Schumacher; also W. G. Pfann and J. H. Scaff, *Trans. A. I. M. E.*, **185,** pp. 383–392, 1949.
3. R. S. Ohl, *Bell System Tech. J.*, Jan., 1952. Also see this paper for more details regarding the method of preparing silicon.
4. H. B. Briggs, *Phys. Rev.*, **77,** pp. 727–728, Mar. 1, 1950.