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FINAL REPORT

ON

INVESTIGATION OF THE OPTICAL PROPERTIES OF

SILICON SOLAR CELL COMPONENT MATERIALS

(Contract No. 952385)

CASE FILE COPY

by

K. Vedam

To

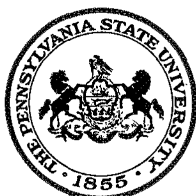
California Institute of Technology

Jet Propulsion Laboratory

4800 Oak Grove Drive

Pasadena, California 91103

5 December 1969



THE MATERIALS RESEARCH LABORATORY

THE PENNSYLVANIA STATE UNIVERSITY

UNIVERSITY PARK, PENNSYLVANIA

FINAL REPORT

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Investigation of the Optical Properties of Silicon Solar Cell Component Materials

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ABSTRACT

Optical absorption coefficient of intrinsic silicon has been determined at a number of discrete wavelengths in the spectral range 400-1000 nm at room temperature. These measurements were also extended to liquid nitrogen and liquid helium temperatures. Results of these measurements in conjunction with our earlier measurements on the refractive index of silicon provide for the first time reliable data on the optical constants of intrinsic silicon and thus form the basis for comparison with similar properties of doped and Li diffused silicon. Irradiation of silicon with 6 MeV protons to fluences of 10^{16} particles/cm^2 does not produce any noticeable change in its optical properties, as determined by techniques involving reflectivity, within the limits of experimental error.

1. INTRODUCTION

The primary objectives of this project are (i) to determine both the real and imaginary parts of the complex refractive index as well as the reflectivity of solar cell quality silicon in the wavelength range 0.4 to 1.1μ, and (ii) to determine the changes in the above optical properties on irradiation by electrons and protons. The results of these studies on intrinsic silicon would form the basis for comparison with the results of similar studies to be carried out later on doped as well as Li diffused silicon, in order to understand the origin and thus possibly find a solution to the degrading behavior of silicon solar cells on irradiation. The first objective was tackled successfully both from the theoretical as well as experimental approach. The results obtained on the theoretical approach have already been reported in the Midway Report dated 21 June 1969. The present report contains the results obtained on the experimental aspect, as well as the results on the effect of irradiation on the optical properties of silicon.

2. STUDIES ON THE OPTICAL ABSORPTION COEFFICIENT OF SILICON

The real part $\underline{n_2}$ of the complex refractive index of silicon could be determined with great precision by measurements on freshly cleaved samples with ellipsometry.[1] However, the same studies showed that the corresponding results on the imaginary part of the refractive index, $\underline{k_2}$, are far from satisfactory. For example, if the value of $\underline{n_2}$ is altered from 4.1401 to 4.1402, then the value of $\underline{k_2}$ must also be altered from 0.020 to 0.009 in order to satisfy a criterion of constancy of the reflectivity R. In other words, in a weakly absorbing material like silicon, it is advisable to use the ellipsometric method only for determining the value of $\underline{n_2}$, and to determine the value of $\underline{k_2}$ it is better to use the conventional direct method of optical absorption technique.

Reference to the literature revealed that the optical absorption of silicon has been studied by Dash and Newman,[2] Braunstein et al.[3] and Runyan.[4] However, there is considerable disparity between the results obtained by these workers as will become evident later in this report.

Silicon has an absorption coefficient of the order $10^3 - 5.10^4$ cm^{-1} in the visible region of spectrum. The loss of light depends mostly on the exponential term e^{-Kd}, where d is the thickness of the sample. To have a reasonable signal in the transmitted light the product Kd should be about 1, and hence d should be in the range 1-10μm. The preparation of such thin experimental samples poses many problems. Theoretically it is possible to calculate the transmitted light energy for non-normal incidence and for a sample with inhomogeneous thickness but such a solution is very complicated and both the mentioned variables (angle of incidence and the thickness) should be known as a function of coordinates x, y in the plane normal to the plane of incidence. A more practical way is to prepare the sample as a plane parallel slab; in such a case the formulae are very simple.

Our samples were prepared by a slightly modified polishing technique of Choyke[5] who developed it for the case of SiC. The procedure adopted was as follows:

(i) A plane parallel slab of vitreous silica was cemented around the periphery to a polishing holder. We used Glass Resin Type 650 (Owen-Illinois Technical Center) as the cement, see Fig. 1 (cement A).

(ii) The upper side of the silica plate was repolished in the usual manner, finishing with 1μm diamond paste. The quality of the surface is not critical because the remaining scratches will be filled with cement with the index of refraction close to the substrate material.

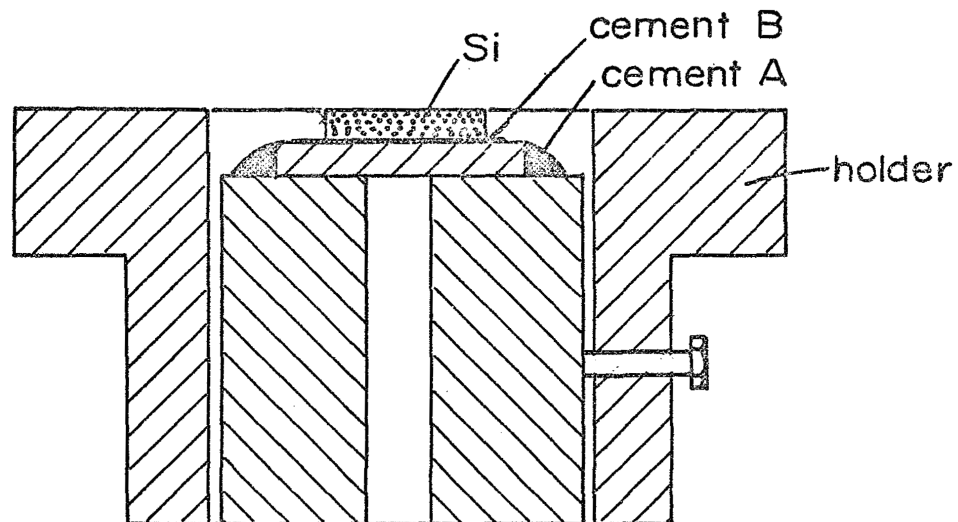

Fig. 1

(iii) The silicon sample was cut from a single crystal (resistivity about 100Ω cm) to the dimensions 5 x 10 mm and thickness 0.5 mm. One side of the sample was carefully polished with 1 μm diamond paste as the final polishing material.

(iv) The silicon sample with polished plane was then cemented to the vitreous silica substrate by Lens Bond Optical Cement Type M62 (Summers Laboratories). The cement was cured by heating the whole holder at 70°C for one hour, during which time a small amount of pressure was applied on Si so the cement film was very thin and both surfaces (Si and the vitreous silica substrate) were parallel to each other.

(v) Then the whole assembly was used to polish the second surface of silicon. During polishing, the thickness of Si was measured by a depth gauge up to 50 μm, and for d<20 μm characteristics of the transmitted light was used for approximate estimation of thickness (20-15 μm sample transmits dark red color, 8-4 μm orange, and 2-1 μm yellow). A coaxial hole in the holder (see Fig. 1) facilitated this procedure. The final stage of polishing with 1 μm diamond paste on silk was very slow and carried out with extreme caution. With an optical microscope it was possible to check with the transmitted light any inhomogeneities in thickness, pinholes and scratches.

The samples used for measurement were free of pinholes with homogeneous density of scratches after 1 μm diamond powder. Inhomogeneities in thickness were mostly on the border of the samples, the central part used for measurement was relatively uniform, but still these inhomogeneities are mostly responsible for the errors in absorption coefficient K. The average thickness was determined from interference of light in near infrared (1-3 μm). This, together with the fact that the K calculated from measurements on different samples in overlapping spectral regions was almost the same, enabled us to estimate the error to be less than 5% in K.

The experimental arrangement employed (Fig. 2) for the measurement of transmission at room temperature consisted of a 250 W tungsten halogen lamp, two Bausch and Lomb grating monochromators (250 mm and 500 mm), PAR chopper, photomultipliers RCA 7102 and EMI 9558, and lock-in amplifier PAR HR8. The transmission was measured point by point as a ratio of signals when sample was in and out of the beam. As we used two monochromators in tandem the scattered light was undetectable. For elimination of second order spectra suitable optical filters were employed.

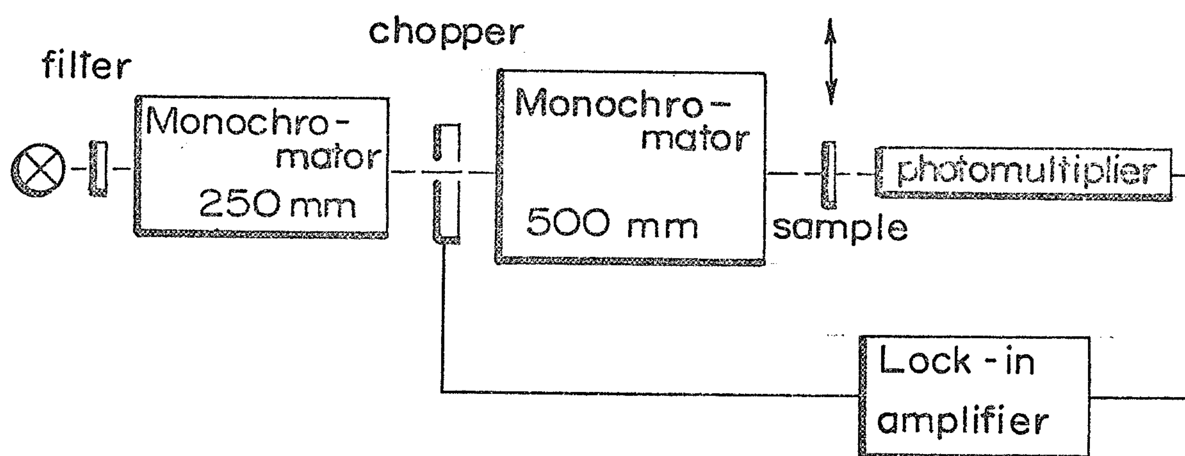

Fig. 2

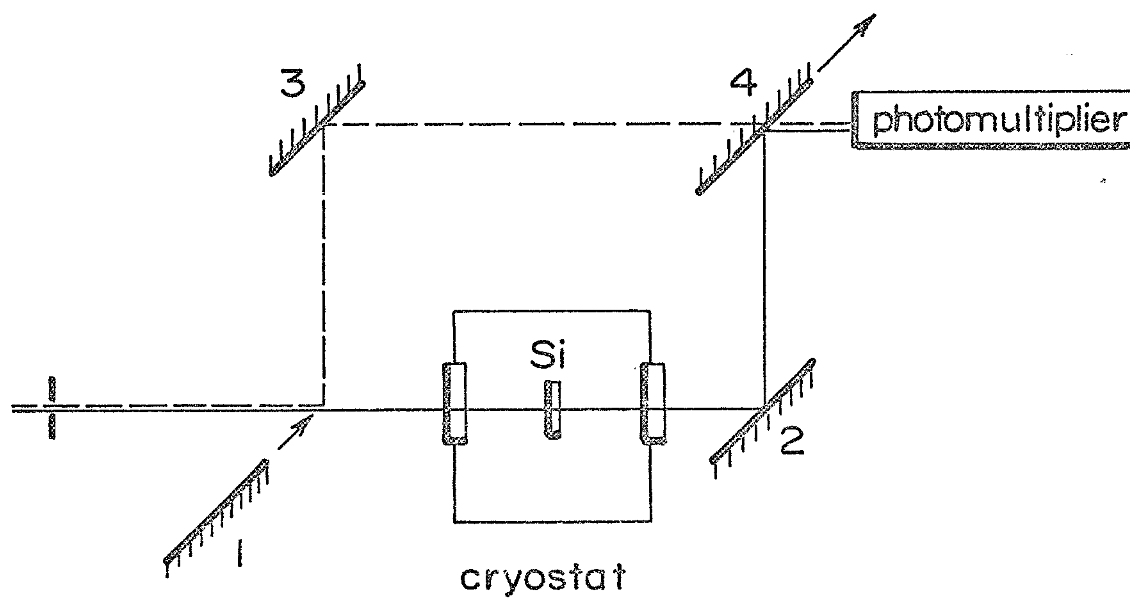

Fig. 3

The experimental arrangement for the measurement at low temperatures was the same except for a slight rearrangement of the optical part behind the second monochromator (Fig. 3). The sample was inside a helium cryostat (Sulfrian Cryogenics) with vitreous silica windows and was cooled to the required temperature by the helium gas. The transmission T was the ratio of signals measured for the optical paths marked with dashed and solid lines on Fig. 3,

$$T = \frac{I_o R_1 R_3 T_W T_{Si}}{I_o R_2 R_4}$$

where I_o is incident light energy and R_i (i=1,2,3,4) reflectance of aluminum mirrors. Both paths are optically equivalent except for the windows, but the correction due to this factor is negligible. Experimentally it was verified that by changing the mirrors, $R_1 R_3 = R_2 R_4$ (difference was less than 1%) and so

$$T = T_W T_{Si} .$$

As the transmission of silicon T_{Si} is known from direct room temperature measurement (Fig. 2) the transmission of windows T_W could be evaluated. As T_W is temperature independent, the T_{Si} for lower temperatures can be determined from the last formula. Here it may be mentioned that the optical components of the experimental arrangement needs careful alignment because the photocathode of a photomultiplier is itself inhomogeneous. Some problems may also arise at low temperature, due to slight distortion of the cryostat.

The absorption coefficient K was determined from a measurement on five samples with average thicknesses of 12.65, 11.29, 4.28, 2.45, 1.01 μm. For final results, a computer program was written by which the absorption coefficient was calculaed approximately from the single reflection formula,

$$T = Ae^{-K_1 d}$$

where

$$A = (1 - R_{01})(1 - R_{12})(1 - R_{23})(1 - R_{34})$$

where $R_{i,(i+1)}$ is the reflectivity of [i, i+1] interface (see Fig. 4)

$$R_{i,i+1} = \left(\frac{N_i - N_{i+1}}{N_i + N_{i+1}} \right)^2$$

N_i is complex index of refraction of medium i. The indices of refraction of air, cement and vitreous silica are known; for silicon we used our earlier reflectance data and the results of K-K analysis.[6] Having thus determined K_1 it was used in the next step, i.e. in the double reflection formula

$$T = A[1 + R_{01}R_{12}e^{-2K_1 d} + R_{12}R_{23} + R_{23}R_{34}]e^{-K_2 d} ,$$

and finally for K by considering the third reflection we have

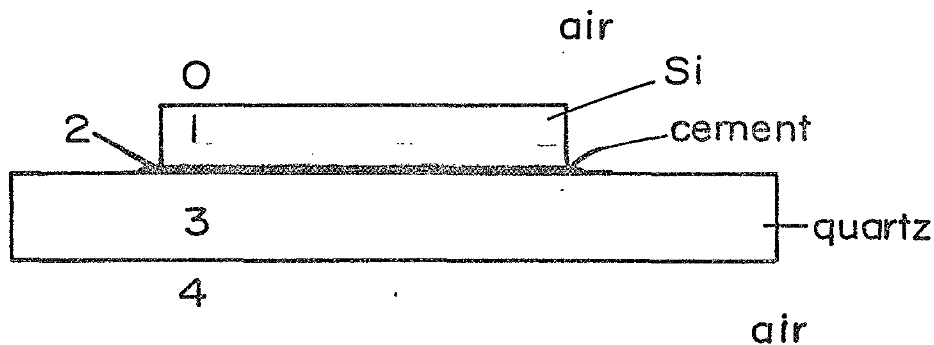

Fig. 4

$$T = A\left\{\left(1 - R_{01}R_{12}e^{-2K_2d}\right)^{-1}\left[1 + e^{-3K_2d}(1 - R_{12})^2R_{01}[R_{23} + (1 - R_{23})^2R_{34}]\right] + \right.$$
$$\left. + R_{12}R_{23} + R_{23}R_{34}\right\} e^{-Kd} .$$

The influence of reflections of higher order is negligible because the difference between K_2 and K was much less than experimental errors.

The final results obtained are shown in Fig. 5. The room temperature data agree very well with those of Dash and Newman.[2] The values obtained by Runyan[4] are slightly lower than ours. At liquid nitrogen temperature (90°K) the agreement with the results of Dash and Newman[2] is good in the region 400-500 nm, for larger wavelength our values are higher. Also, we did not observe the weak dip in K close to 2.4 eV (510 nm) at liquid nitrogen temperature, as reported by Dash and Newman.[2] In the literature this structure has not been observed by other workers as well, e.g. the reflectance measurement at different angles of incidence[7] and high sensitivity electroreflectance.[8] From a theoretical calculation, Herman et al.[9] predicted the direct absorption edge at 2.8 eV but other authors[10] found theoretically first direct transitions close to 3.4 eV which was experimentally confirmed. The data of Braunstein et al.[3] at room temperature are very close to ours and at liquid nitrogen temperature between the data of Dash and Newman[2] and ours. These results[3] also do not show the dip close to the 2.4 eV but as their last measurement is at 2.5 eV this argument cannot have much weight.

Further, the measurement at liquid helium temperature (about 9°K) does not show any anomalous behavior of K at 2.4 eV. The relative shift of K curves with temperature is the same as the shift of the indirect energy gap (at 1.1 eV) as reported by McFarlane et al.[11] within the experimental error at 700 nm.

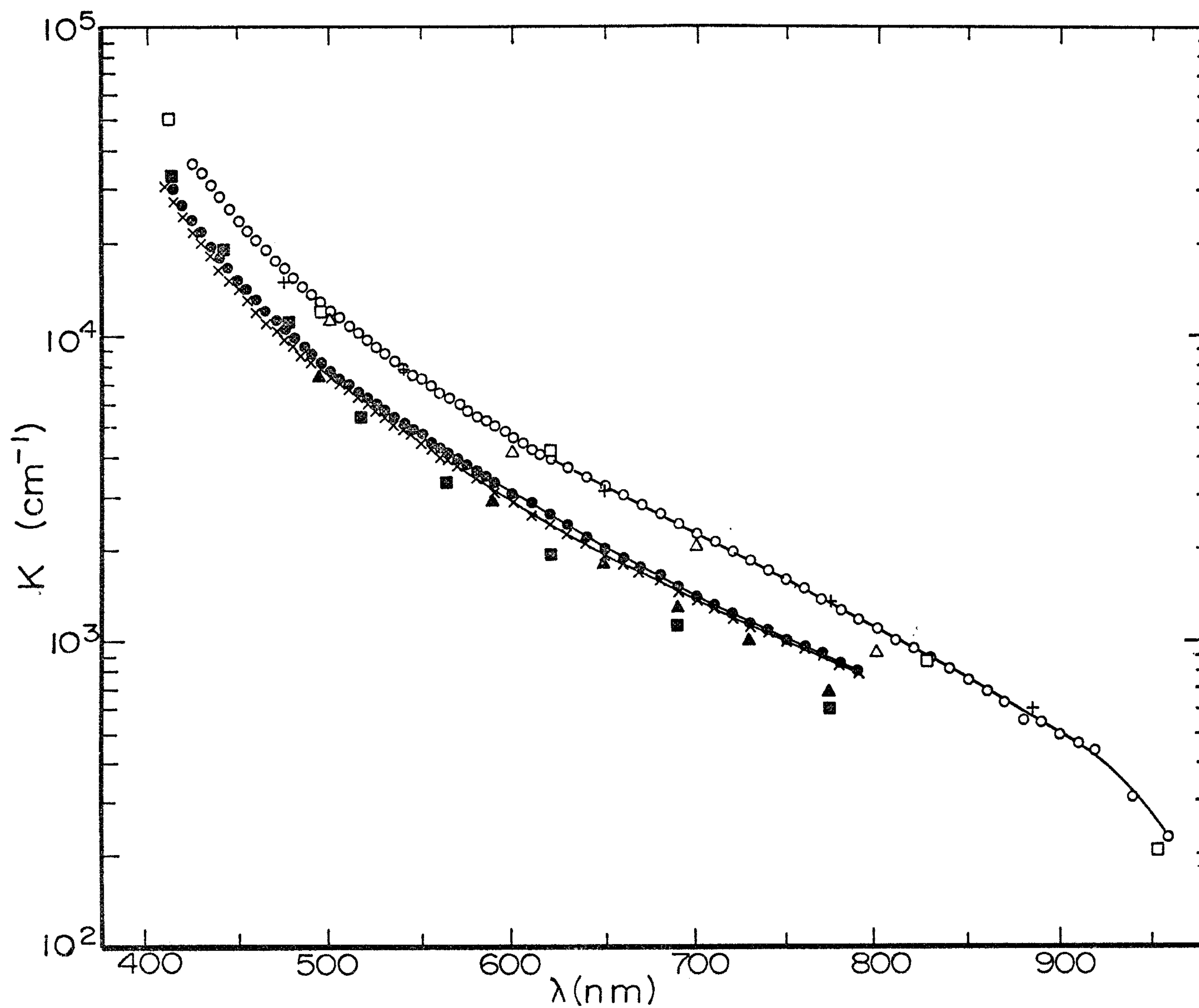

Fig. 5

Absorption coefficient of silicon vs. wavelength. Our results o—o—o (300°K); ●—●—● (90°K); x—x—x (9°K). Dash & Newman[2] □ (300°K); Braunstein et al.[3] + (296°K); Runyan[4] Δ (300°K).

3. STUDIES ON RADIATION DAMAGE

The effect of irradiation of 6 MeV protons on the optical properties of intrinsic silicon was studied by two different methods: namely (i) ellipsometry to measure any changes in the real and imaginary components of the refractive index of silicon and (ii) direct measurement of the change in reflectivity of silicon by a sensitive modulation technique. The results obtained on both these studies are given below.

A. Ellipsometric studies: Five samples of intrinsic Si were cleaved along the (111) plane by the Gobeli-Allen technique[12] to give optically plane areas of several square millimeters each. Each sample was then thermally oxidized for a different length of time at 950°C to yield a range of SiO_2 surface film thicknesses from 34Å to 3840Å.

The ellipsometric parameters Δ and ψ of each sample were measured prior to its insertion into a custom fitted holder for proton irradiation. The ellipsometric parameters were again measured after exposure to 6 MeV protons at a fluence of 10^{16} particles/cm^2. This maximum specified fluence and energy were chosen for this series in order to first determine the maximum effect on the optical constants. During irradiation particular care was taken to prevent excessive heating of the specimen by irradiating them at low dosage rate as well as to have the specimen holder cooled by running water during irradiation. The results of this series of measurements are shown in the accompanying Table No. I. The ellipsometric parameters Δ and ψ are determined by the index of refraction and thickness of the surface film and by the optical constants of the substrate material. No change in Δ and ψ was observed which could have been caused by a change in the optical constants of the substrate. The only observable change was

Table I

Ellipsometric Parameters Before and After Irradiation

Sample #	Before Irradiation		After Irradiation		Changes Observed as Result of Irradiation
	Δ	ψ	Δ	ψ	
RD-1	165.39°	12.24°	161.02°	12.32°	Film thickness increased from 53Å to 62Å; no observable change in the optical constants.
RD-2	169.12°	11.86°	168.47°	11.96°	Film thickness increased from 34 to 36Å; no change in the optical constants was observed.
RD-4	272.54°	57.95°	274.16°	54.79°	Film thickness increased from 3840Å to 3865Å; again no observable change in the Si substrate optical constants.
RD-5	113.78°	18.23°	107.85°	19.84°	Film thickness increased from 278Å to 323Å; no observable chance in the substrate optical constants.
RD-6	88.00°	28.48°	87.00°	29.13°	SiO_2 film increased in thickness from 566Å to 585Å. There was no change observed in substrate optical constants.

due to a change in SiO_2 film thickness, the magnitude of which is dependent on the degree of heating during irradiation.

Thus we conclude that 6 MeV protons of fluence 10^{16} particles/cm^2 are not sufficient to cause a change in the substrate optical constants as determined by reflection-type optical measurements.

B. Reflectivity measurements: For the measurement of small changes of reflectivity R caused by radiation damage, a simple experiment based on modulation technique was designed. A sample of Si of circular cross section was first mechanically and later chemically polished by the standard procedure. Later, during irradiation two diagonally opposite quadrants of the sample were masked off with absorbers as shown in Fig. 6. For the measurement of the change in R the sample was mounted in a rotating holder (ω=26 Hz), and a narrow pencil of light reflected from a quadrant of the sample was detected by a photomultiplier coupled appropriately to a lock-in amplifier. The experimental arrangement was similar to that used for the measurement of absorption. The ac signal was proportional to the difference in the reflectance of irradiated and unirradiated parts of sample. The limiting sensitivity of the method was determined by the mechanical vibrations which caused moving of the light spot on the inhomogeneous photocathode; this spurious signal was about 0.1%. The energy of protons was 6 MeV, fluence 10^{16} proton/cm^2. The measurement of reflectance in the energy interval 1-5 eV gave only negative results - the change in reflectivity was smaller than 10^{-3} which is the limit of this method and experimental arrangement.

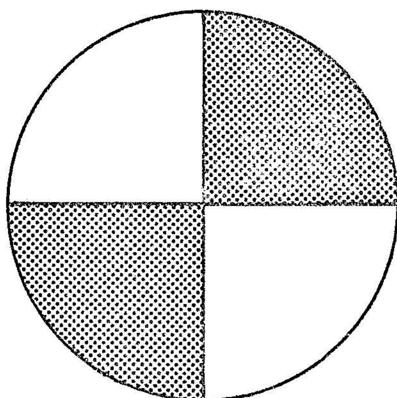

Fig. 6

4. CONCLUSIONS AND RECOMMENDATIONS

Reliable values of both the real and imaginary parts of the complex refractive index of intrinsic silicon have now been obtained. Irradiation with 6 MeV protons to fluences of 10^{16} particles/cm^2 does not produce any noticeable changes in the optical properties of silicon within the limits of experimental error, as can be detected by techniques based on reflection.

These studies form the basis for comparison with similar studies that should be carried out on highly doped silicon of the type used in silicon solar cell fabrication. Again the effect of diffusion of lithium, which is known to affect the reflectivity of the material, should be investigated along similar lines. Effect of irradiation with electrons on the optical properties of silicon and doped silicon, though not carried out in the present work for want of irradiation facilities, should be studied. Only then will we be able to understand the origin of the degradation properties of silicon solar cells on irradiation and thus possibly develop ways and means to overcome them.

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