A STUDY OF THE ABSORPTION COEFFICIENT OF SILICON IN THE WAVE LENGTH REGION BETWEEN .5 AND 1.1 MICRONS

FINAL REPORT

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by

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INTRODUCTION

The goal of this study was to examine the absorption coefficient of silicon in the wavelength region from 0.5 to 1 micron as a function of doping level and crystal damage in order that solar cell performance might be better predicted. In this light there are several areas of interest. Among them are:

1) Does the heavy doping in the diffused layer cause absorption processes which do not produce hole-electron pairs? If so, it could lead to an alternate explanation for the poor short wavelength spectral response of cells.
2) Does the heavy doping required for built-in electric fields affect the efficiency because of a large free carrier absorption? (Since the inception of this work, drift field cells have been proven of little merit, so the importance of this aspect is now greatly reduced.)
3) What is the effect of the strain associated with polycrystalline depositions on the absorption process and on the efficiency of hole-electron production?
4) Does residual damage left in thin silicon solar cells contribute to the decrease of efficiency with thickness which is greater than that predicted by simple theory?

EXPERIMENTAL PROCEDURES

The absorption coefficient was calculated directly from transmission data. Optical equipment used for this purpose consisted of a Perkin-Elmer Model E-1 monochrometer, a 0.38 to 1.05 micron grating, a Perkin-Elmer sample holder, and a 12 volt incandescent bulb with reflector and collimating lens as a source. The monochrometer is a single beam instrument and was used in its double pass mode with an internal chopper. When operating in this manner, the specification quotes the percent light scattering in the instrument as 10^{-4} percent.

The detection system was an RCA type 7102 photomultipler (usually cooled to dry ice temperature) and a PAR Model HR-8 amplifier and phase detector. In order to prevent ground loops from introducing spurious signals into the amplifier from the monochrometer's internal reference signal generator, a 240 CPS line frequency synchronized chopper was used and the PAR reference signal generated by quadrupling the line frequency.

Since the instrument is single beam, a sample in /sample out test procedure was used. Ordinarily, sample holders with identical limiting apertures were used in pairs so that the rather fragile samples did not have to be repeatedly removed and replaced from their holders as the frequency was traversed.

The thin samples required were obtained by a variety of methods which are tabulated below.

1. "Microweb" material from Dow Corning. These were available in miscellaneous thicknesses greater than 15 microns, and with various resistivities between 0.1 and 200 Ω-cm.
2. By direct polishing, either mechanical or chemical, the whole slice to the desired thickness.

3. Chemically thinning the center of a slice.
4. By oriented overgrowth onto a sapphire substrate. This latter method has some attendant potential difficulties which will be discussed later and so must be used with caution.

Calculations for the silicon-only samples were made in a straightforward manner from the expression.

$$I/I_o = (1-R)^2 e^{-\alpha x} / 1-R^2 e^{-2\alpha x} .$$

Where R is the silicon-air reflection coefficient, x is the sample thickness, and α the absorption coefficient of silicon. In most instances, because of the large value of α, the denominator was assumed to be one. Values of reflectivity were obtained from Taft and Phillip.[1]

For the silicon-on-sapphire samples, the approximate expression

$$I/I_o = (1-R_1) (1-R_2) (1-R_3) e^{-\alpha x}$$

was used where

R_1 = reflection coefficient at the air-silicon interface

R_2 = reflection coefficient at the silicon-sapphire interface

R_3 = reflection coefficient at the sapphire-air interface

<u>Errors</u>

Sources of error in determining the absorption coefficient appear to be predominately due to:

1. Thickness variations in the slice
2. Minor variations in reflection coefficient
3. Instrumentation error.

Light leakage and scattered light were assumed to be negligible.

Since $\alpha = (1/t) \ln\left[\frac{(I_o/I)}{(1-R)^2}\right]$, error in the measurement of t leads immediately to a similar size error in α. Thicknesses were determined by direct measurement using microscope and bifilar eyepiece; by infrared interferometry using a modified Beckman IR5A; and in the case of deposition on sapphire, by step etch and a Talysurf profilometer. For cases where the thickness was uniform, thickness measurement error should not exceed 5%. Unfortunately, in the present study non-uniform films probably contributed more in some cases, and in addition is considerably less amenable to determination since it will vary from sample to sample. Efforts were made to minimize the effect by examining the films under transmitted light with an optical microscope and choosing regions for measurement which appeared to have uniform transmission characteristics.

Minor variations in reflection coefficient and errors in intensity readings can be lumped together and considered in terms of the error produced in the (absorption coefficient) · (thickness) product determination versus the ratio of I to I_o. In general this indicates that as α decreases, t must increase in order to maintain a constant error. However, since one of the goals of this study was to observe a given sample over a wide range of absorption coefficients, variations in t were minimized. It is therefore of interest to consider what effect fixed errors in determining I/I_o (which may be due either to instrument errors or variations in surface reflection) have on the αt products as αt is varied. This is illustrated in Figure 1 for the specific case of an error of I of ±5%. A 5% instrument error is about the smallest that could be expected. Thus, for a sample thickness of 10 microns, α must be greater than 400 for a total error of less than 10%. However, for a 100 micron sample, alphas of above 40 could be determined to the same accuracy. It is believed that this is the reason for the wide variation in values in the long wavelength region.

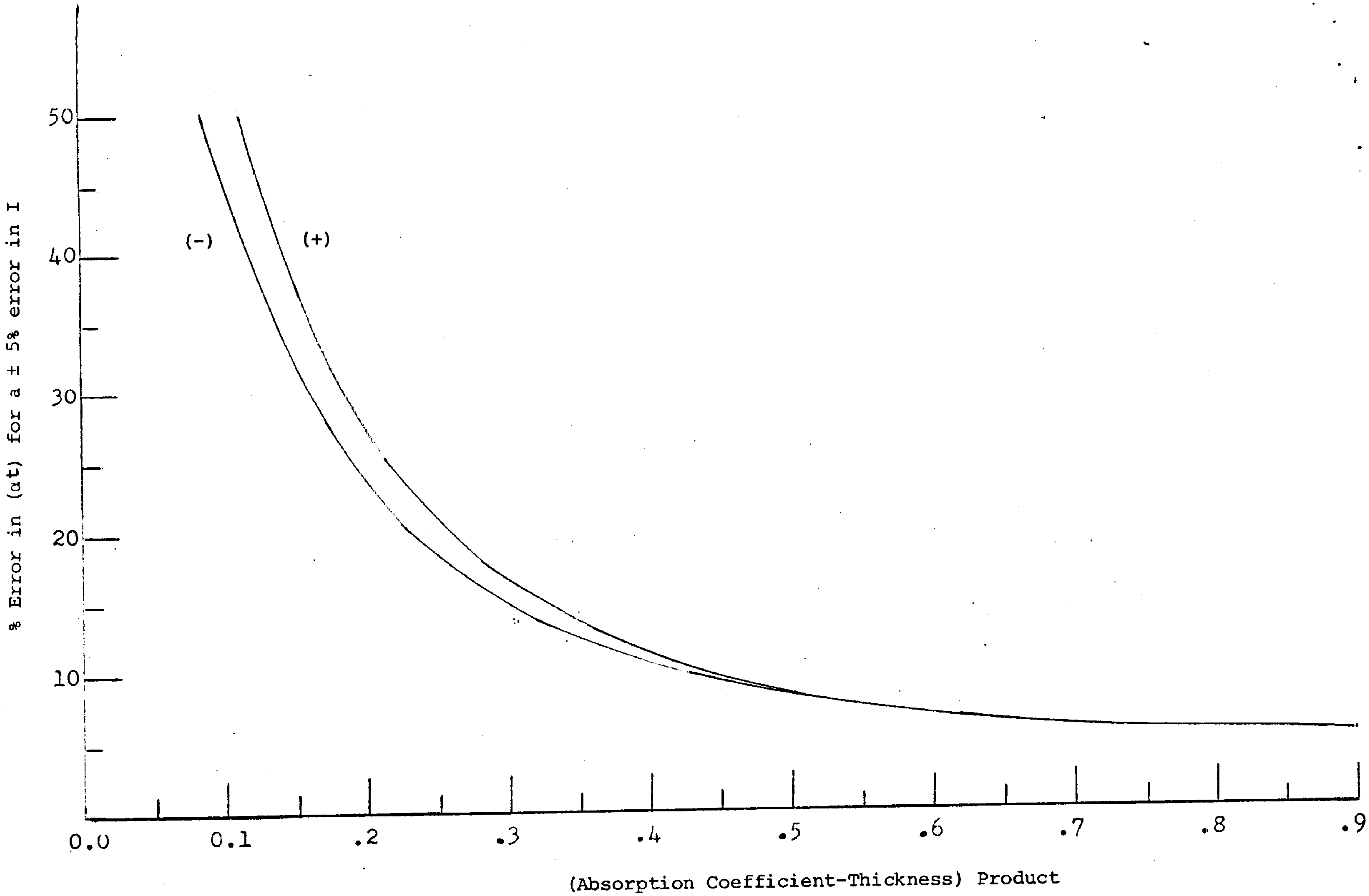

Fig. 1. Error in absorption coefficient caused by error in transmissivity.

EXPERIMENTAL DATA

The data taken can be logically divided into three categories, the results of which are shown in Figures 2, 3, 4, and 5. The first category, as represented by Curve C of Figure 2, is a re-examination of the absorption coefficient of relatively pure silicon with damage free surfaces. Curves A and B are two sets of previously published data and are included for comparison.[2,3] For wavelengths shorter than 0.9 microns the new data is approximately 20% lower than either of the others. Several possible reasons for this discrepancy present themselves. One is that the thickness was mismeasured. Since it is really an absorption coefficient thickness product that is experimentally determined, a constant thickness error would cause a constant absorption error. Present data covers thickness ranges from 7 to 100 microns as measured variously by I.R. interferometry, Talysurf, Calibrated microscope eyepiece, and movable stage tool makers microscope. It does not therefore seem likely that this is the problem. However, the literature data were taken at different times in different laboratories so it is doubtful that they would both have made the same thickness error. Examination of the curves also shows that if the wavelength scale were shifted approximately 0.02 microns, the data would agree quite well. In order to check this possibility the calibration of the spectrometer used in this study was checked after the experiments were completed and was found to be in order. Dispersion effects caused by wide slits and the large dependance of alpha could produce a shift, but this also appears unlikely.* It has been shown that in the case of GaAs, strain in the crystal, induced either by thermal mismatch with a substrate, or due to cutting and polishing damage, can increase the absorption coefficient [4]. Both Dash and Newman[2]

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* For this instrument, the spectral line width at 0.5 microns is .005 microns for the maximum slit width of 1 cm.

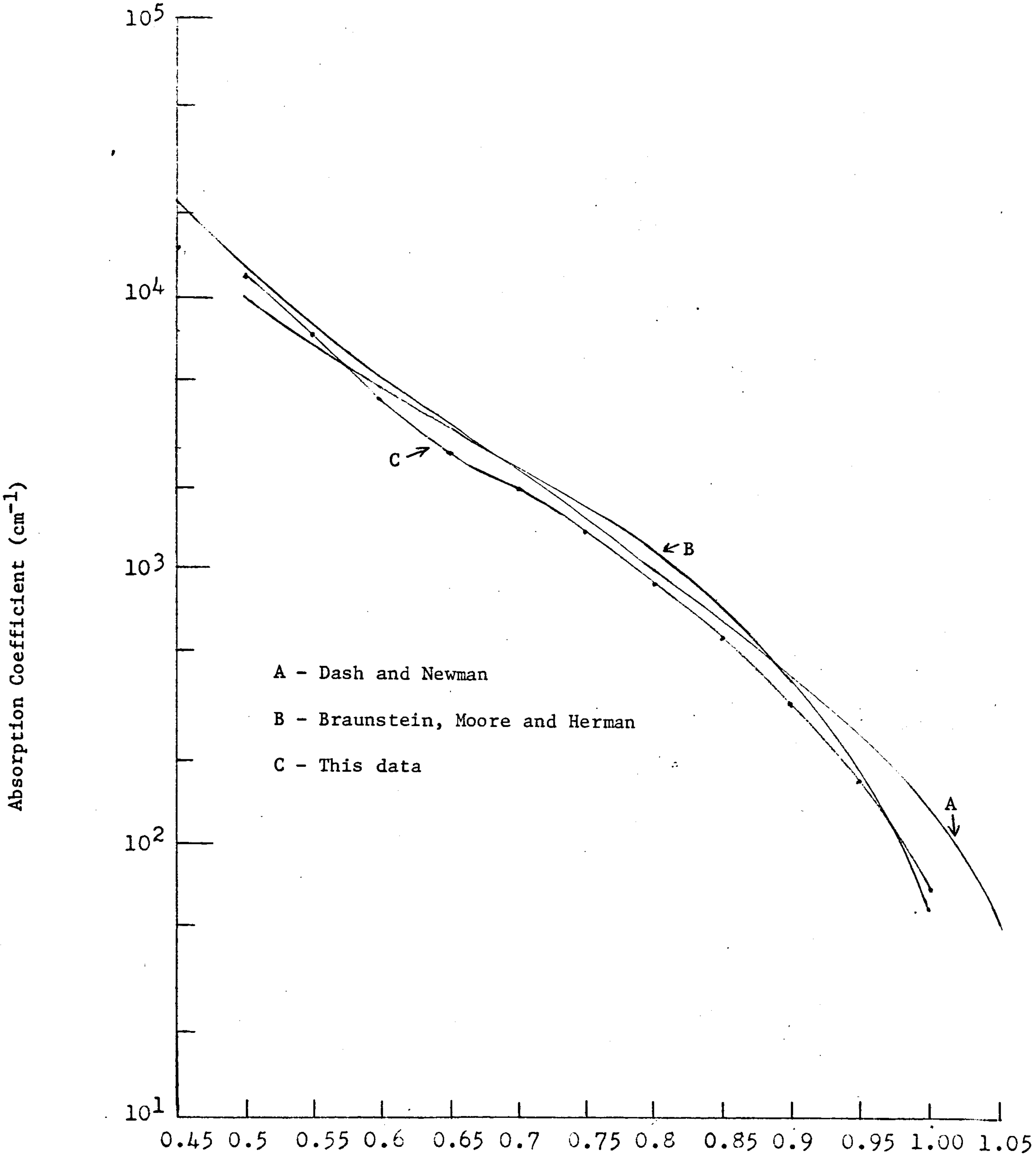

Fig. 2. A Comparison of Silicon Absorption Data.

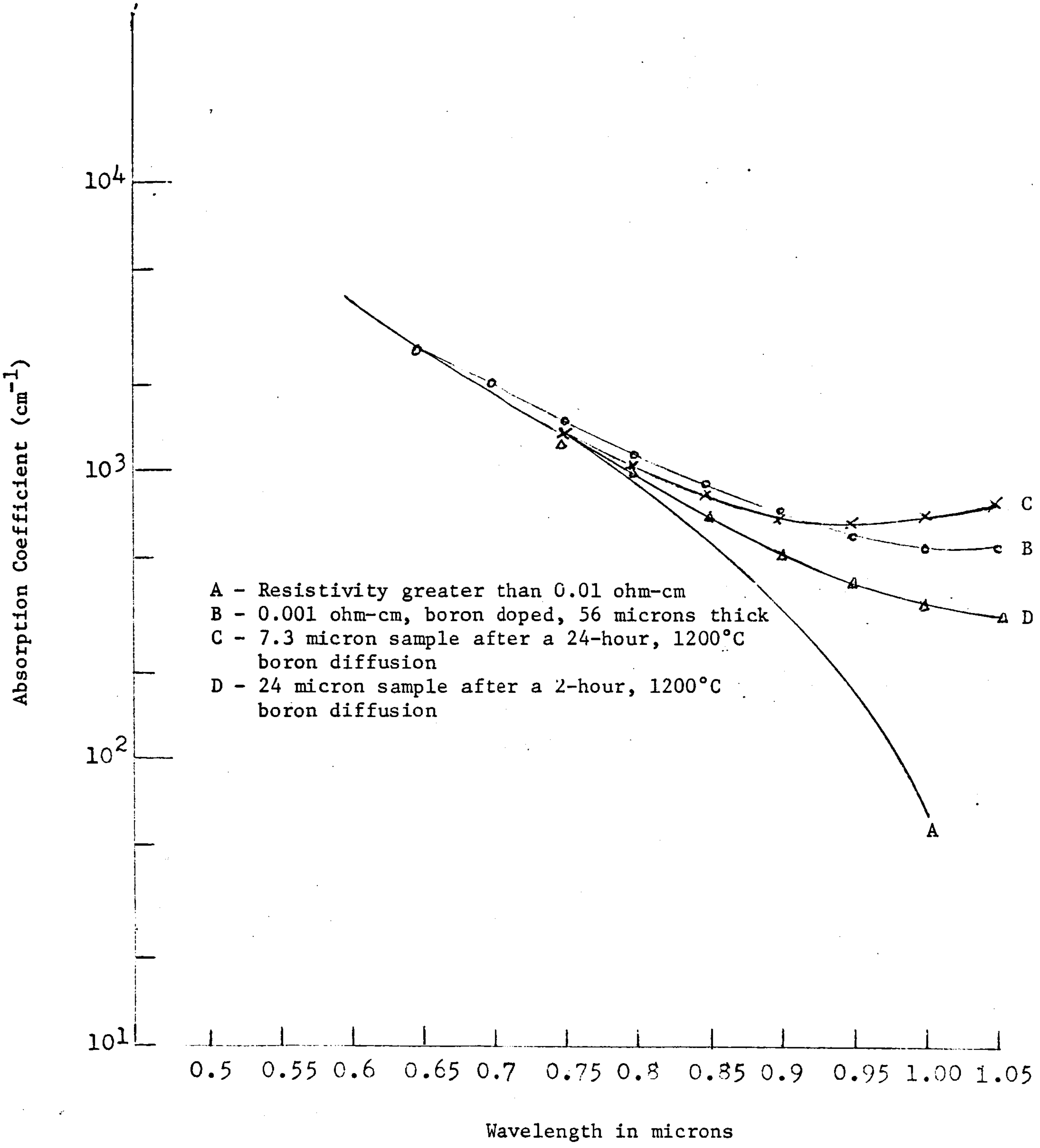

Fig. 3. Effect of Doping on Absorption Coefficient.

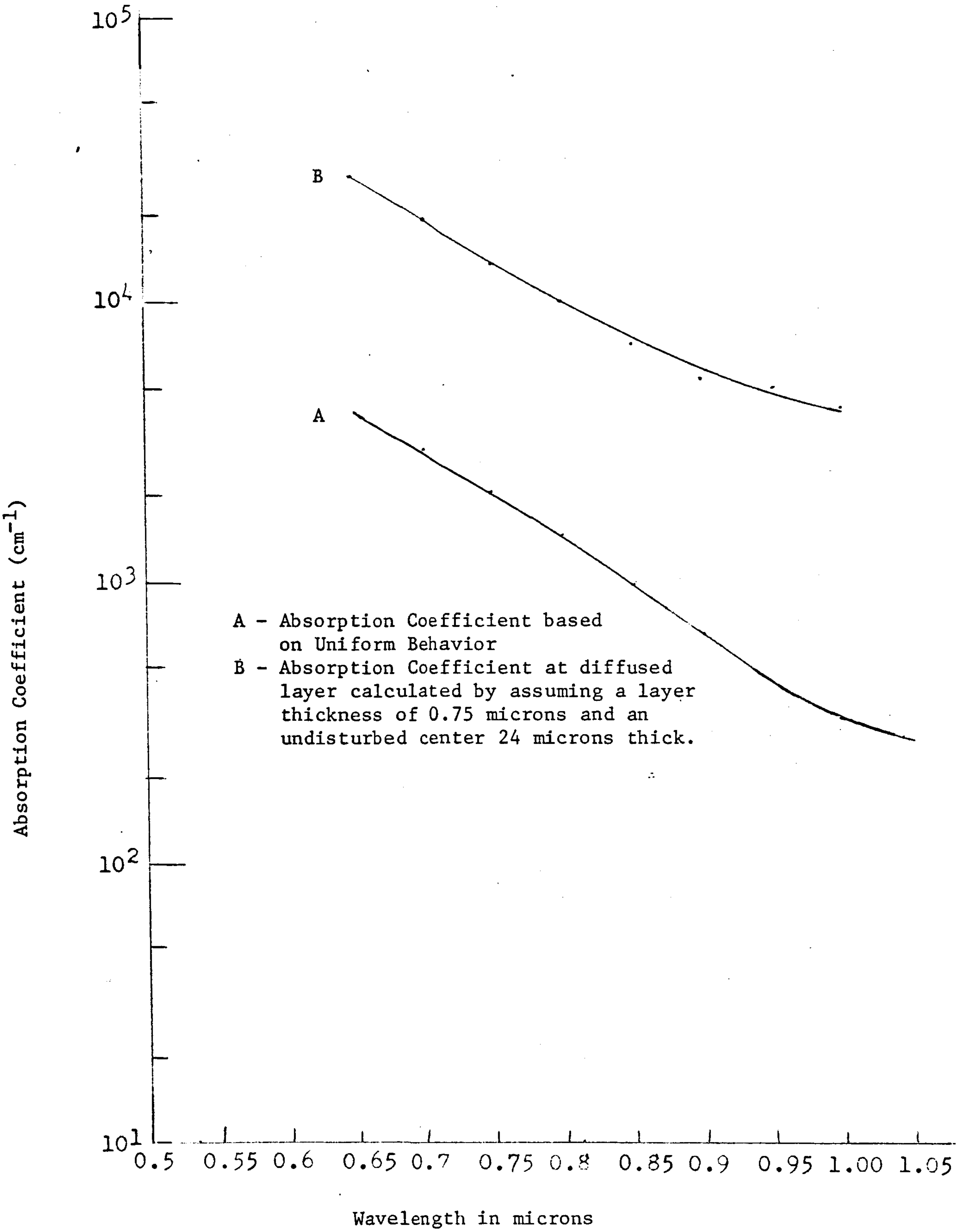

Fig. 4. Absorption Coefficient for 0.01 ohm-cm web after a boron diffusion.

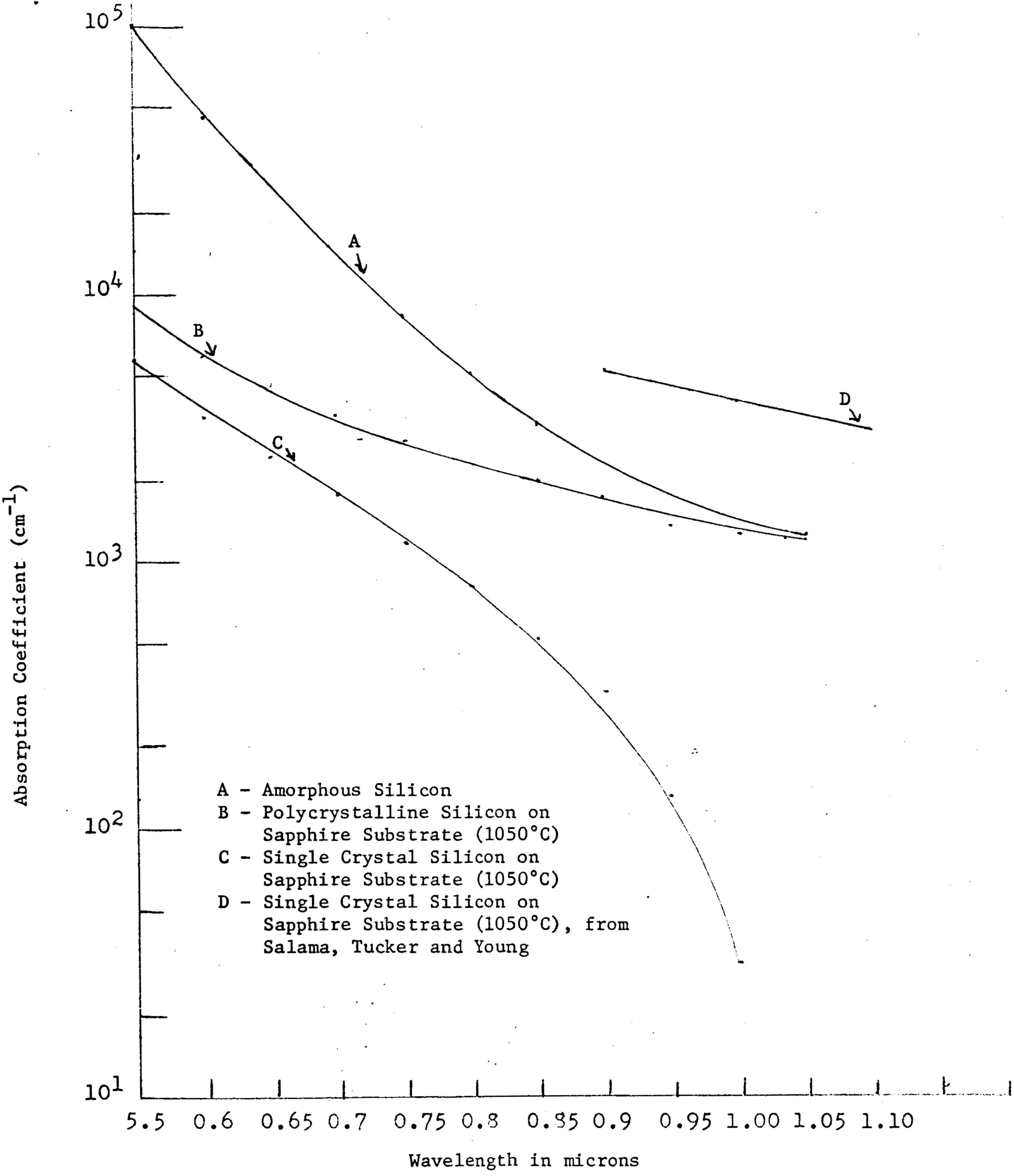

Fig. 5. Effect of Structure on Absorption Coefficient.

and Braunstein, Moore and Herman used mechanically polished surfaces whereas the present work has been either with web (<u>no</u> surface processing) or with chemically polished surfaces in which every effort was made to remove as much of the previously mechanically induced damage as possible.* It appears likely that the present study used samples under less strain than the previous workers, but unfortunately time has not permitted definitive experiments relating actual absorption coefficient changes with strain.

The second category of experiments examined the effect of relatively heavy doping on the absorption coefficient. For wavelengths longer than band edge, these effects have been considered in detail[5-7] and in general show an approximate squarelaw wavelength dependence and an increase in alpha with doping level. Figure 3 shows the high purity curve from the previous figure, that for a 0.001 ohm-cm born doped sample (curve B), a sample that had been boron diffused for twenty-four hours (curve C), and a sample with a short boron diffusion (curve D). This latter sample was 24 microns thick and had a diffused layer approximately 0.7 micron thick on each side. The "effective" absorption coefficient shown was calculated on the basis of uniform composition and so is less than either curve B or curve C.

Curve B, and presumably any other intermediate between it and Curve A, can reasonably well be described by adding to Curve A a component of alpha due to free carrier absorption which can be measured in the longer wave length region and assumed to vary as wavelength squared. Curve B represents material with approximately 10^{20} boron atoms /cc. The concentration of boron in the material of Curve C is somewhat non-uniform and has a surface concentration of between 5 and 10×10^{20} atoms/cc. The behavior of this curve appears somewhat different than that of Curve B and may be due to

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* For a summary of data used for Curve C, see Appendix I.

surface layer of varying optical properties. The possibility of the latter is illustrated by the data of Figure 4A which shows the absorption coefficient for one sample of web which presumably had a two hour 1200°C boron diffusion. No other samples were found to show this behavior, but this particular sample was measured several times and did indeed have an extraordinarily high absorption coefficient. Examination after a Sirtl etch showed excessive crystallographic damage. Viewed through crossed infrared polarizers no excessive strain was noted, however, such an instrument is very insensitive. Optical transmission microscopy showed a multitude of opaque "dots" which did not appear to have blocked off enough area to give rise to the large apparent absorption coefficient. Figure 4, Curve B, shows the results of calculating an alpha based only on the supposed 1.5 microns of diffused layer (with the remainder of the thickness having a normal absorption coefficient). As will be shown a little later, this very large coefficient is not unlike that of a heavily damaged layer.

Figure 5 contains the results of the third category of studies. This set of curves shows the effect of polycrystalline silicon on the absorption coefficient. Curve C is for single crystal oriented overgrowth onto a sapphire substrate and is virtually the same as Curve C of Figure 2. Curves A and B are respectively for a polycrystalline sample and an amorphous evaporated layer.* Curve D is from the literature and represents a polycrystalline sample.[8] It should be noted that similar effects have been observed for Germanium[9] and GaAs samples.[10] A comparison of Curves B and D with that of Figure 4B shows a not unreasonable agreement.

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*The single crystal sample and the polycrystalline sample were courtesy Dr. W. Tefteller of Texas Instruments Incorporated and were deposited from a silane-hydrogen mixture at a temperature of 1050°C.

EFFECT OF FINDINGS ON SOLAR CELL CALCULATIONS

Doping heavy enough to cause appreciable free carrier absorption in the 0.8 to 1.0 micron region will normally only occur in the diffused layer at the front of the cell. Since the layer is quite thin, the number of photons lost to this process is quite small. For example, a layer thickness of one micron with an absorption coefficient of 800/cm will transmit 92% of the total intensity. Further, since wavelengths longer than 0.8 microns account for no more than 25% of the total photocurrent collected, the total reduction in current due to the absorbing layer will be less than 2%. If for some reason thicker regions of heavily doped material is used, then the effect must be calculated for the particular case.

Of more speculative interest is the possibility that because of the solar cell diffusion, there is an extremely thin layer formed which has an absorption coefficient like that of Figure 4 rather than the more typical one of Figure 3. If this were so, a layer 0.1 micron thick would absorb a large fraction of the photons of wavelength shorter than 0.5 micron. By further assuming that the new absorption process does not produce carriers, an alternate explanation for the lack of short wavelength silicon solar cell response is provided. (Present theory presumes that the phenomenon is due either to an exceedingly short lifetime in the diffused layer[11] or to the effect of the built-in internal field of the diffused layer.[12]) It should be noted however that there is evidence that for germanium at least, extensive lattice disorder* smears interband transitions but does not necessarily introduce any new absorption processes.[9]

This same phenomenon of an alpha increasing as the polycrystallinity increases is also of considerable interest in predicting the behavior of thin

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* For the specific case of diffused layers, the possibility of a highly absorbing second phase such as silicon boride or phosphide forming at the surface should not be ruled out.

polycrystalline silicon solar cells. If for instance the alpha increase noted in going from curve C to curve B of Figure 5 were due to a non-carrier producing process, then clearly polycrystalline cells could never be as good as single crystal ones, even if the mobility, carrier lifetime and junction quality were all comparable. Alternately, if the absorption process does generate a carrier for each polycrystalline, silicon would be required to absorb the majority of the sun's energy. However, in a recent study of gallium arsenide solar cells[10], it was found that only material whose optical properties closely approximated those of single crystals was useful for solar cells, though the reason for failure was attributed to the very high resistivity also associated with the highly disordered and highly absorbing film.

One remaining item to be considered is the effect of the somewhat reduced absorption coefficient at each wavelength on the calculated cumulative absorption curve. It was originally believed that the lower absorption coefficient data of Figure 2 might predict an appreciable change in the cumulative absorption curve that had previously been used for cell calculations. This in turn could have helped explain the discrepancy between the calculated and experimentally observed performance of thin silicon cells[14]. However, spot computations have indicated that the measured change would not appreciably affect those results.

CONCLUSIONS

It is concluded that the details of the revised absorption coefficient curve do not differ enough from previous data to warrant any re-examination of theoretical single crystal solar cell behavior. However, the phenomenon of a higher absorption coefficient in small crystallite polycrystalline semiconductors could be further studied and might perhaps shed new light on the behavior of polycrystalline photovoltaic and photoconductive devices.

APPENDIX I

	A	B	C	D	E	F	G	H	I
0.45					15,200				15,000
0.50					13,300				13,000
0.55					7,500				7,500
0.6	3500			4000	4,200		3700	4600	4,100
0.65	2350	3000	2900	2800	2,600		2750	2950	2,800
0.70	1500	2500	2100	1900	2,000		1900	2000	2,000
0.75	1100	1400	1400	1300	1,300		1300	1400	1,350
0.80	710	890	890	880	860	820	890	910	880
0.85	4000	560	550	560	500	510	590	580	550
0.90	250	330	320	340	250	300	360	350	330
0.95	110	160	170	170	98	150	200	170	170
1.0	75	57	61	70		60	77	78	67
1.05		4.4				6.9	32		

A - n-type web 200 Ω-cm, 20 microns thick
B - 10^{-15} Ω-cm boron doped 45.7 microns thick
C - 10^{-15} Ω-cm p-type 45.7 microns thick
D - 4-6 Ω-cm n-type, 15 microns thick
E - 4-6 Ω-cm n-type, 7.3 microns thick
F - 6 Ω-cm antimony doped web, 108 microns thick
G - 08 Ω-cm web p-type, 24.6 microns thick
H - rerun of G
I - Values used for curve C of Figure 1.

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