Submitted to Physica Status Solidi

LBL-3751
Preprint

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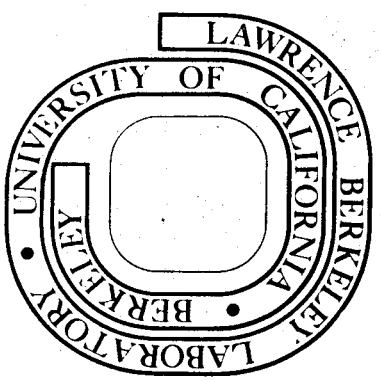
March 1975

Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48



DISCLAIMER

APPLICATION OF THE RIGID-BAND MODEL TO THE ENHANCEMENT/QUENCHING EFFECTS IN HEAT-TREATED Cu_xS/CdS HETEROJUNCTIONS

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ABSTRACT

The non-linear effects observed in the short-circuit current response of air-heat-treated Cu_xS/CdS cells when illuminated simultaneously by two light sources of different wavelengths are explained in terms of the rigid-band model of Cu_xS proposed by B. J. Mulder [3]. The mathematical model developed to explain the quenching of short wave length response by long wavelength secondary light is shown to give good agreement with published data.

AUSZUG

Die nonlinearen Effekte im Kurzschluss-Strom in Luft wärmebehandelter Cu_xS/CdS Zellen, die man bei gleichzeitiger Beleuchtung mit zwei verschiedenen Wellenlängen beobachtet, werden erklärt im Rahmen des "Starre-Bänder" - Modelles, das B. J. Mulder [3] für Cu_xS vorgeschlagen hat. Ein mathematisches Modell wird entwickelt welches - in guter Übereinstimmung mit Daten in der Literatur - die Unterdrückung des Kurzwellen-Kurzschluss-Stroms durch langwelliges Licht erklärt.

1. INTRODUCTION

Several workers have reported non-linear, short-circuit current spectral response effects in cadmium sulfide solar cells [e.g., 1-3]. These effects have been ascribed to trapping at impurity levels in the CdS [1,2] or to a modulation of the conductivity of a high resistivity interfacial layer [3]. In earlier work the non-linear effects seemed to show up erratically [1], but more recently it has shown that, with proper care in junction fabrication, they appear only after heating in an oxidizing environment [2,4]. It will be demonstrated in this paper that the occurrance of these effects is consistent with the rigid-band model of Cu_xS proposed by B. J. Mulder [5]; and that many of the features of these effects can be accounted for in terms of this model without recourse to localized trapping levels.

2. THE RIGID-BAND MODEL

The rigid-band model of Cu_xS assumes that the dependence of electron energy on wavevector E(k) near the band gap in chalcocite (Cu_2S) and djurleite ($Cu_{1.95}S$) is approximately as shown in Fig. 1. Also indicated in Fig. 1 are the gap energies for direct (E_{gd}) and indirect (E_{gi}) transitions, and the positions of the fermi levels in the two phases. Notice that in chalcocite both valence bands are nearly full so that its absorption characteristic exhibits both an indirect "edge" at about 1.2 eV and a stronger, direct "edge" at about 1.8 eV [6]. However, since the fermi level in djurleite lies well below the $k\neq 0$ (indirect) valence

band maximum, there are very few electrons in that band; and photons of energies less than E_{gd} cannot cause many transitions to the conduction band. Therefore, the presence of this band is almost imperceptible in monochromatic absorption measurements [e.g. reference 6].

3. THE ENHANCEMENT EFFECT

Consider, however, what happens when djurleite is illuminated by short wavelength light ($\lambda \gtrsim E_{gd}$). There will be many transitions from the "direct" (i.e. maximum at k=0) valence band to the conduction band followed by recombination of the excited carriers. Notice that initially the indirect band is almost "full" of holes so that many of the excited electrons may "drop" into that band instead of returning to the direct band. Thus, the effect of this short wavelength light is to populate the indirect valence band; in other words, it raises the temperature of the valence band electron distribution. Then, if the characteristic time for inter-valence band transitions is comparable to, or longer than, that for conduction band-valence band transitions,* a relatively small intensity of short wave length light will be sufficient to maintain this high-temperature distribution.

Given this "bias" illumination, the adsorption characteristic of djurleite should be quite similar to that of chalcocite. That this is indeed the case can be seen in Fig. 2 which shows short-circuit current

*A very likely hypothesis, considering the result, mentioned in reference [2], that long dark periods (10^3 sec. at room temperature) are required to regain the pre-enhanced state.

(S.C.C.) response curves for chalcocite, djurleite and $Cu_{1.9}S$ back-wall cells calculated using the absorption constants given by Mulder, [6] together with experimental response curves [reproduced from reference 7] for a backwall CdS cell before and after heat treatment. Comparison of the calculated curves with the measured monochromatic response after heat treatment leaves little doubt that the Cu_xS layer has undergone a phase transformation from chalcocite to a lower-x phase.* However, as shown, the addition of simultaneous, short wavelength "secondary" illumination restores the original response curve shape--shifted down by roughly a factor of four possibly because of the increased lattice mismatch, as suggested in reference [8].

4. THE QUENCHING EFFECT

Now consider what happens when light of energy $\simeq E_{gi}$ is added to short wavelength illumination of a djurleite cell. The presence of the longer wavelength light will enhance the rate of minority carrier transitions to the indirect valence band because of stimulated emission. The long wavelength light will also be strongly absorbed by carriers already in the indirect valence band. The net effect then will be a

*The logarithmic plot tends to exaggerate the differences at the smaller currents. It should be noted that the calculated response curves depend on a rather indirect determination of the optical constants (see Ref. [6]); and that, in particular, the slop of the djurleite curve for $\lambda \gtrsim 0.7\mu m$ is due to a small interband absorption component extracted numerically from a large free-carrier absorption term. Furthermore, very small amounts of stray light could have caused the long wavelength absorption to appear much larger than it would otherwise (for exactly the reasons being discussed here).

small increase in the total S.C.C.* However, one may separate the responses of the cell to the primary and secondary illumination by chopping the primary beam, as did Gill [7]. Then one finds that the A.C. component of the S.C.C. is decreased as the unchopped secondary light intensity is increased.

The explanation of this phenomenon in terms of the rigid-band model is as follows: The long wavelength seconary light causes large numbers of transitions between the indirect valence band and the conduction band in both directions - "up" because of absorption, of course, and "down" because of stimulated smission. This means that there is an increased overall likelihood of a given carrier's arriving at the junction after excitation to the conduction band. But the probability of its arriving without having made at least one transition to the indirect band and back is diminished in direct proportion to the secondary intensity. Thus the effect of the secondary is to smooth out the arrival rate of carriers generated by the chopped primary by "storing" them in the indirect valence band. This process has been modeled mathematically by noting that the inverse of the minority carrier lifetime τ will increase proportional to the secondary light intensity I in the case of stimulated emission:

$$1/\tau = \frac{1}{\tau_o} \quad (1 + AI) \qquad (1)$$

*Under some conditions there may be a small net <u>decrease</u> in .S.C.C. because of the increased losses due to inter-valence band transitions.

where A is a constant of proportionality. Further, the secondary intensity will be a strong function of position satisfying the differential equation,

$$dI/dx = -\kappa(x)\ I \tag{2}$$

where $\kappa(x)$ is the absorption coefficient of secondary at x in the presence of short wavelength primary illumination. Then the one-dimensional diffusion equation for the minority carrier concentration n (at the primary chopping frequency) can be written as:

$$D(d^2n/dx^2) - n(1+AI)/\tau_o = -k_1\Phi e^{-kx} \tag{3}$$

where D is the carrier diffusivity, k_1 and k are the primary wavelength inter-band and total absorption coefficients respectively, and Φ is the incident primary intensity.

To avoid the additional complication of solving coupled differential equations, we make the somewhat crude assumption that $\kappa(x)$ has the form,

$$\kappa(x) = \kappa_o e^{-kx} \quad . \tag{4}$$

That is, we assume that the absorption of secondary, which is known to be very weak in the absence of primary light, decays with the intensity of the primary. This assumption allows Eq. (2) to be solved:

$$I = I_o \exp[\kappa_o/k(e^{-kx}-1)] \quad . \tag{5}$$

Equation (3) has been solved numerically* using Eq. (5) and the usual boundary conditions $n(0)=n(\infty)=0$. The resulting value of dn/dx at $x=0$ is linearly related to the A.C. component of the S.C.C. It was found that by proper choice of the three adjustable parameters involved [$A, kL_o=k(D\tau_o)^{1/2}$, and κ_o/k] that very good agreement with the data presented by Gill [7],** could be attained, as shown in Fig. 3.

5. DISCUSSION AND CONCLUSIONS

The comparison between calculated and experimental monochromatic S.C.C. response characteristics shown in Fig. 2 suggests the non-heat-treated cell consists of mostly chalcocite while the heat-treated cell has been largely converted to another cuprous sulfide, probably djurleite. Then the enhancement effect and the restoration of a chalcocite-like response in the presence of a "bias" illumination are necessary consequences of the rigid-band model.

There is perhaps too little data for one to draw any quantitative conclusions from the fit shown in Fig. 3, since small amounts of scatter could lead to errors in the "best fit" parameter values. In fact, the value of kL_o used in Fig. 3 was determined by choosing $L_o=0.1\mu m$, a value found to give reasonable agreement with experiment for

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*Actually, the equation solved was that resulting from making the change of variable $z \equiv e^{-kx/2}$ in Eq. (3). This has the advantage of making the boundary conditions easier to handle on the computer.

**Error bars shown were inferred from Gill's statement that his light intensity measurements were of ±20% accuracy, p.31.

spectral response calculations [Cf. ref. 8]; and using $k=8\mu m^{-1}$, approximately the value reported by Mulder [6] for photons of wavelength ~5600Å. However, it is encouraging that parameter A, which is a measure of how effectively the secondary stimulates conduction band-indirect valence band transitions, seems to decrease as the secondary wavelength increases; because there will be fewer transitions possible with a lower energy secondary and hence, a lower total transition probability. The third parameter κ_o/k was introduced to decouple Eqs. (2) and (3); and it is not as clearly related to physical properties as the others. To achieve good fits, it seems κ_o/k must be at least of order 10, as in Fig. 3. This would seem to indicate [see Eq. (4)] very strong attenuation of the secondary near the junction; which seems incongruous with the relatively small measured absorption coefficient, even in chalcocite, at the secondary wavelength [6]. However, this high value may only indicate the model is too crude with respect to the assumption regarding $\kappa(x)$ (Eq. 4). Notice that a more detailed model should admit the possibility of $\kappa(x)$ being negative for large primary intensity and small x.

Further testing and refinement of this model is clearly in order. The most obvious refinement is the elimination of the assumption necessary to decouple Eqs. (2) and (3). This would result in the introduction of physically more meaningful parameters to replace κ_o/k. However, more detailed, <u>quantitative</u> experimental data is necessary to properly test the predictions of such a model. The present body of data is largely qualitative and deals almost exclusively with defining the

wavelength regions associated with these effects, whereas the testing of the model demands precise data on the variations in the intensity dependences as well.

6. SUMMARY

In summary, the rigid band model of Cu_xS seems capable of accounting for the non-linear, two-beam effects found in heat-treated Cu_xS/CdS cells in a straightforward manner: They are absent in the case of chalcocite cells (distinguishable by their strong monochromatic response to wavelengths of about .95-1.0μm) because the direct valence band maximum lies well below the Fermi level. However, in djurleite cells the Fermi level has moved down to the top of the direct band. Then enhancement of long wavelength response by short wavelength light is caused by redistribution of valence band electrons, leaving some of them in the indirect valence band where they may absorb the long wavelength light in a transition to the conduction band. Finally, quenching of short wavelength response is due to the increased transition rate of carriers to the indirect valence band because of stimulated emission in the presence of the long wavelength light.

ACKNOWLEDGEMENTS

The author wishes to thank Professor Leo Falicov for several very helpful discussions and suggestions; and Professor Jack Washburn for his encouragement and support on this project. This work was supported by the U.S. Energy Research and Development Administration through the Inorganic Materials Research Division of the Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

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FIGURE CAPTIONS

Fig. 1. Rigid band model for chalcocite (Cu_2S) and djurleite ($Cu_{1.95}S$).

Fig. 2. Comparison of experimental and calculated spectral response curves of back-wall Cu_xS/CdS cells. Experimental curves (broken lines) are from Ref. 7 and show typical responses of the same cell (called "cell #1" in [7]) before and after heat treatment (1 min. at 250°C in air). Note that the response for $\lambda \lesssim 0.54\mu m$ is complicated by the CdS absorption which was not considered in the calculated curves. The solid curves are calculated from the solution of the one-dimensional diffusion equation plus Mulder's [6] absorption data and an assumed minority carrier diffusion length of 0.1μm. The djurleite and $Cu_{1.9}S$ curves were arbitrarily shifted down by a factor of 0.25 (see text and ref. 8).

Fig. 3. Quenching of chopped primary response vs. secondary intensity. The abscissa is the square root of I to be consistent with Gill's format [7]. $kL_o = 0.8$; $\kappa_o/k = 15$. Primary wavelength = 5640Å. Experimental data from [7].

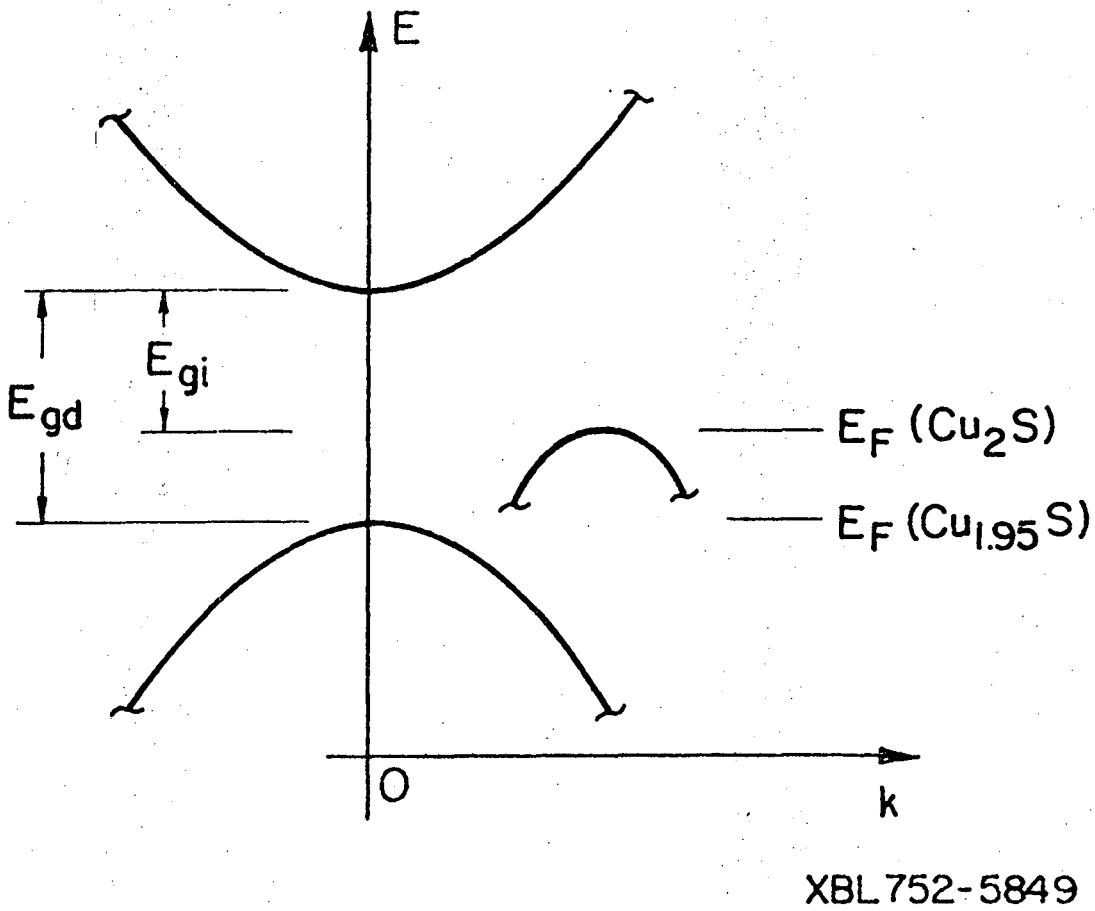

Fig. 1.

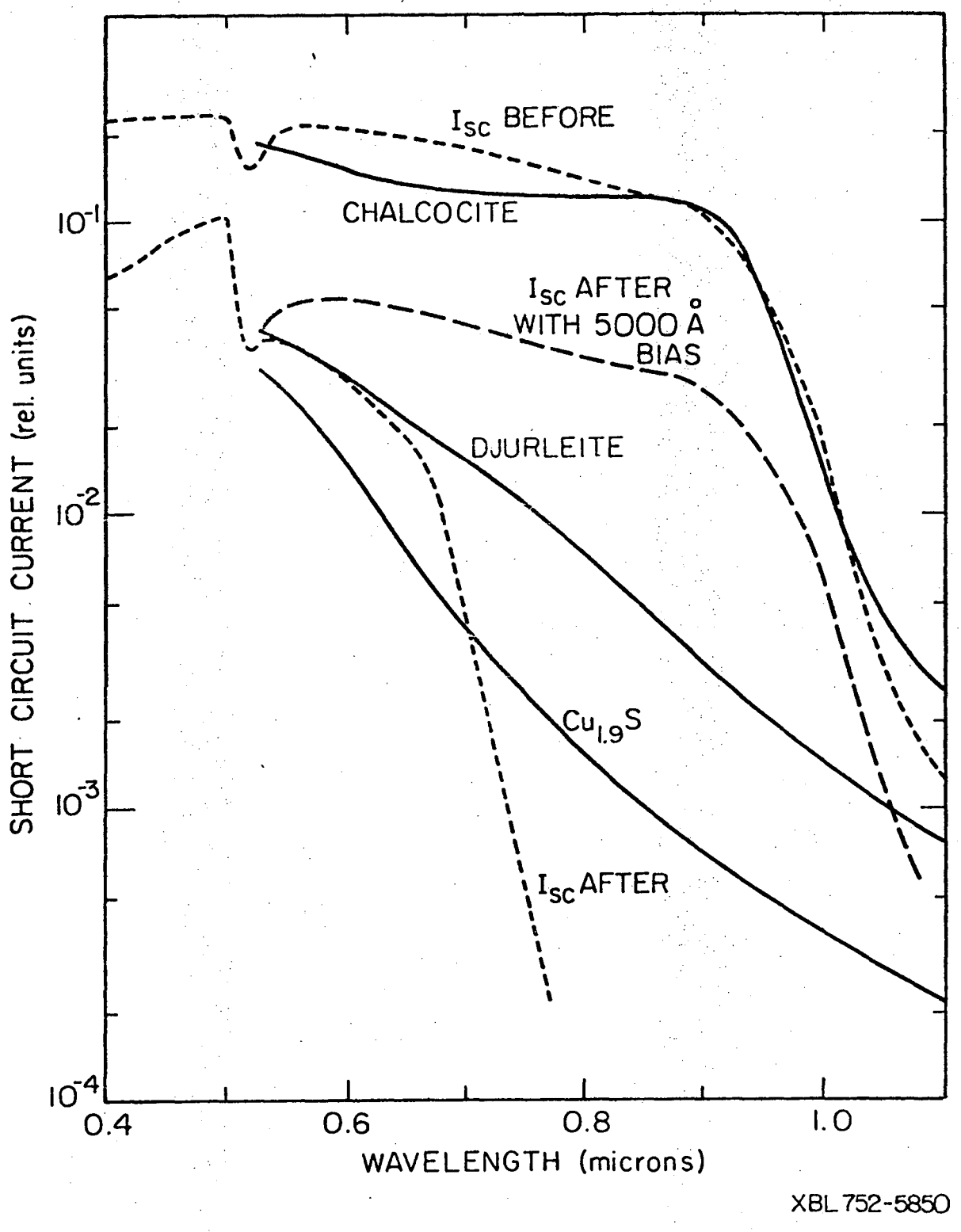
I_{sc} BEFORE
CHALCOCITE
I_{sc} AFTER WITH 5000 Å BIAS
DJURLEITE
$Cu_{1.9}S$
I_{sc} AFTER
SHORT CIRCUIT CURRENT (rel. units)
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0.4
0.6
0.8
1.0
WAVELENGTH (microns)
XBL 752-5850

Fig. 2.

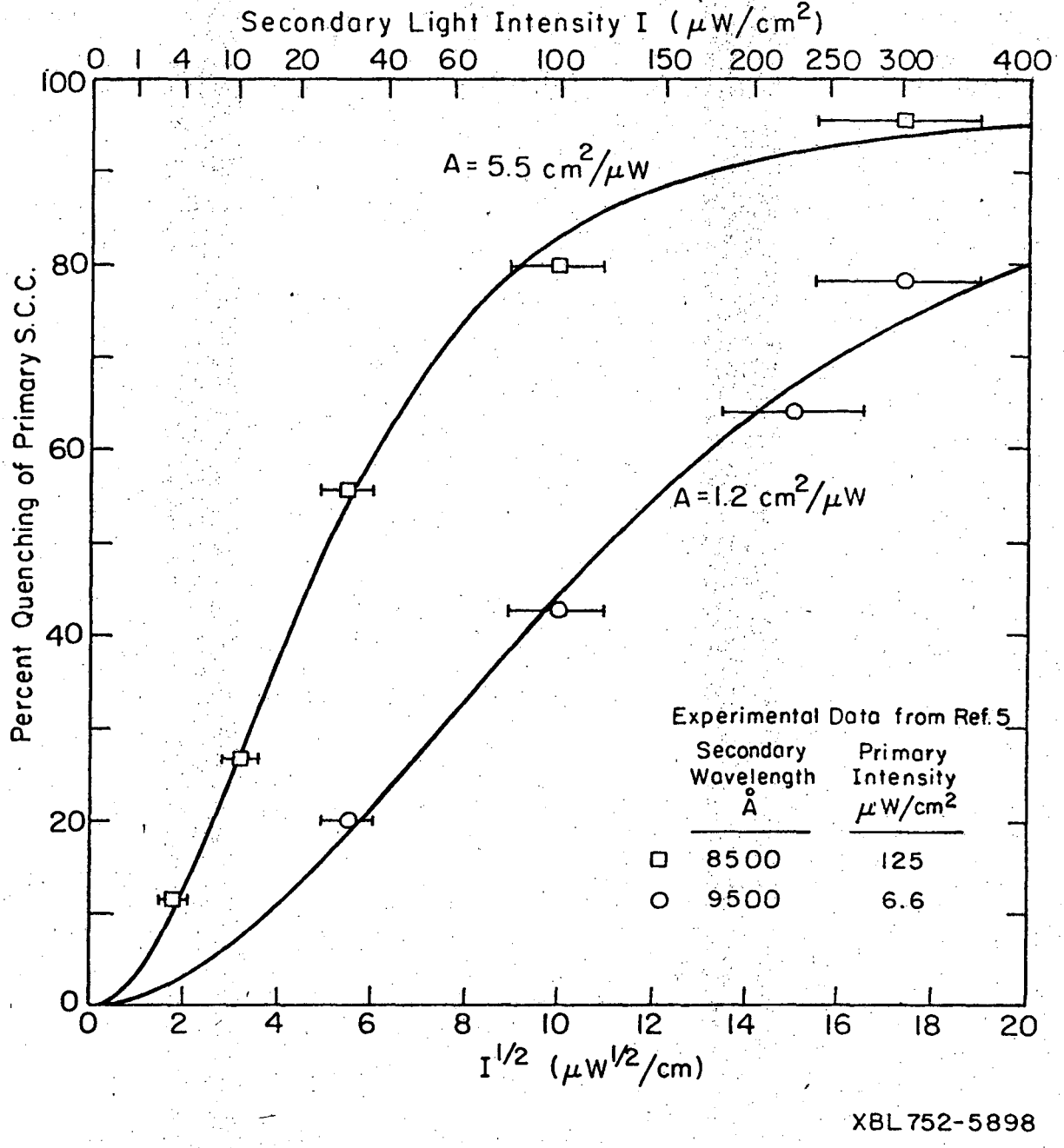

Fig. 3.

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