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New approach to the analysis of thermally stimulated conductivity measurements applied to zinc-compensated silicon*

Sameh A. Rabie
Department of Electrical Engineering, McGill University, Montreal, Quebec, H3C 3G1, Canada
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An extensive analysis of thermally stimulated conductivity (TSC) measurements in zinc-compensated silicon samples has been carried out in order to obtain information about their trapping structure. The measurements were analyzed with the help of available TSC techniques, augmented by four newly developed concepts, which are based on the influence of the following effects on TSC spectra: (i) illumination intensity, (ii) recombination lifetime, (iii) trap filling mechanism, and (iv) resistivity inhomogeneity. The usefulness and importance of the above-mentioned concepts as well as of other older techniques are discussed in a manner that is applicable to the general analysis of TSC and thermoluminescence data. The detailed analysis of ordinary as well as of decayed TSC measurements, performed on serveral n-type zinc-compensated silicon samples containing approximately 10^{16} cm^{-3} of arsenic and having room-temperature resistivities between 3 and 150 $k\Omega cm$, indicate the existence of five discrete traps located approximately 0.1, 0.14, 0.19, 0.41, and 0.36 eV from the edge of the conduction band. The first four levels all empty by fast retrapping mechanisms whereas the last is a slow trap. It is thus demonstrated that the use of our additional techniques for the analysis of TSC measurements even in seemingly complicated situations such as zinc in silicon, yields a much clearer picture on the trapping structure in materials than was previously possible.

I. INTRODUCTION

Both thermally stimulated conductivity (TSC) and thermoluminescence (TL) methods have been extensively used for studying trapping phenomena in a wide variety of materials over the past three decades.[1,2] Analysis of TSC and TL curves shows that the role played by a trap is largely dependent on the relative probability of freed carriers recombining with carriers of opposite type at some recombination center, or being captured back at trap sites.[3] Therefore, knowledge of the type of trapping is important, not only because it ultimately determines the role played by a trap in any photoconductive application,[4] but also because without this knowledge a complete and reliable evaluation of the TSC and TL data is not possible.

The theory of TSC and TL has been the object of numerous investigations[3,5] which have resulted in the development of fairly general mathematical theories for TSC[6] and TL[7] in the presence of one set of fast or slow traps, for both cases of constant and varying lifetime. However, the problem of deducing trapping parameters from the measured TSC and TL spectra is generally difficult and often fraught with uncertainty.[8,9] Not only is the analysis usually complicated by the presence of several traps[1,2] and by sample inhomogeneity,[10] but also by the absence of prerequisite information on the type of trapping kinetics, as well as on the temperature dependence of recombination lifetime, thus making the choice of the appropriate model for analysis in many cases rather arbitrary.

In many practical situations, the temperature dependence of lifetime may be estimated from either a knowledge of the recombination properties of the crystal under investigation and/or from an independent measurement of the variation of the steady-state photoconductivity with temperature. Information about the type of trapping, however, is usually difficult to obtain. In order to overcome this problem, some authors suggested methods of TSC and TL analysis that do not require an *a priori* knowledge of the type of trapping.[5,11,12] These methods, however, yield only the trap depth, leaving the other trap parameters and properties unknown. The few attempts at evaluating the type of trapping kinetics[8,13,14] have been shown to have in general limited practical usefulness.[3,15]

The present investigation is aimed at solving some of the difficulties which are normally associated with TSC analysis, with particular emphasis on the problem of characterizing the trapping kinetics. Following a discussion of the conditions of applicability of the most frequently used TSC techniques, we present a detailed analysis of our TSC measurements in several zinc-compensated silicon samples. The measurements are analyzed using existing TSC techniques, as well as the results of our recently published work on the effects of illumination intensity,[15] recombination lifetime,[16] and inhomogeneity[10] on TSC spectra. In addition, a newly developed approach which is based on studying the mechanism of trap filling in order to determine the type of trapping kinetics is presented and applied to our results.

The paper could thus serve two purposes. The first is to yield information about the trapping structure of zinc-compensated silicon. This is particularly important in the light of the potential

of this material in optoelectronic application,[17] and because of the existing wide scatter in published data on several of the material's properties.[18] The second purpose is to give some new insight into the usefulness and limitations of existing as well as new techniques which may be used for TSC analysis. In fact, the systematic approach we adopt for analyzing the complex TSC spectra of zinc-compensated silicon could be of help to many investigators who might be using the TSC-TL method for studying the trapping properties of any material.

II. GENERAL PROPERTIES OF TSC CURVES

A. Basic theory

The basic model for TSC analysis assumes the presence of one discrete set of traps (we will assume single acceptors), and one set of recombination centers.[19] In cases where more than one type of trap are present, it is assumed either that the TSC currents due to different traps occur at well separated temperatures, or that decayed TSC experiments[6] have been carried out in order to obtain isolated peaks. The solution due to Haering and Adams[5] for the TSC curve and the position of the peak T_m can be written in the following general form,

$$\sigma(T) = q\mu N_c \eta_0 \frac{\tau}{\tau_1} \exp\left(-E_t/kT - \int_{T_0}^{T} \frac{N_c}{N_t \beta \tau_1} e^{-E_t/kT} dT\right), \quad (1)$$

$$e^{E_t/kT_m} = \frac{N_c k T_m^2}{N_t \beta E_t \tau_1} , \quad (2)$$

where $\sigma(T)$ is the thermally stimulated conductivity at the temperature T; q and μ are, respectively, the electronic charge and mobility; η_0 is the relative initial trap population $N_t^-(0)/N_t$, where $N_t^-(0)$ is the density of filled traps at the excitation temperature T_0, and N_t is the total density of traps; τ is the free-electron lifetime; E_t is the trap depth; N_c is the effective density of states in the conduction band, and β is the linear heating rate. The meaning of the parameter τ_1 depends on the ratio of the recombination time τ to the trapping time $\tau_{tr} = (\beta_{tn}^0 N_t)^{-1}$, where β_{tn}^0 is the electron capture coefficient of neutral traps. For fast trapping ($\tau_{tr} \ll \tau$), $\tau_1 \equiv \tau$, whereas for slow trapping ($\tau_{tr} \gg \tau$), $\tau_1 \equiv \tau_{tr}$. In the analysis of Haering and Adams, the variations of N_c, μ, τ_{tr}, and τ with temperature have been ignored. It has also been assumed that the illumination intensity is sufficiently weak that the traps are left sparsely populated at the excitation temperature ($\eta_0 \leq 0.1$).

In cases where the illumination intensity is high ($\eta_0 \sim 1$), the analysis of Haering and Adams remains valid for slow traps. However, in the case of fast traps, the TSC model is nonlinear and Eqs. (1) and (2) become inaccurate. Our numerical solution for $\sigma(T)$ in that case[15] shows that, in the presence of a large trap population, the width of the TSC peak substantially increases, and the initial rise portion of the TSC curve becomes more curved. Another feature is that the position of the TSC peak becomes a function of the relative trap population at the peak η_m, and the expression for the peak T_m analogous to Eq. (2) becomes

$$e^{E_t/kT_m} = N_c k T_m^2 / N_t \beta E_t \tau (1 - \eta_m)^2 . \quad (3)$$

However, the shift of the peak temperature T_m due to the variation of illumination intensity has been predicted to seldom exceed a few degrees. In cases where T_m is reproducible so that small shifts in T_m could be detected with reasonable accuracy, the effect of illumination intensity could be used as a tool for identifying the type of trapping kinetics.

From the above it can be seen that for low illumination intensity ($\eta_0 < 0.1$), the TSC curves will have the same features for both types of trapping.[20] This, however, does not make it unnecessary to determine the type of trapping before any reliable evaluation of the TSC data can be undertaken. If, for instance, a peak due to a slow trap is wrongly interpreted as being due to a fast one, it can be proved that the trap depth will be overestimated, whereas the opposite is true when a fast trap is wrongly interpreted as a slow one. The resulting error is a function of the ratio τ/τ_{tr} and may be quite significant in practical situations.

An important point worth mentioning here, is that if a fast trap is wrongly assumed to be a slow one and Eq. (2) is used to calculate the capture coefficient β_{tn}^0, it can be proved that the resulting value of β_{tn}^0 will always be much less than the true value. Therefore a procedure that has been advocated by some authors[3,21] whereby one begins the analysis by assuming that a trap is slow, and subsequently uses the calculated value of β_{tn}^0 to verify the initial assumption is a questionable procedure.

B. Effects of lifetime and inhomogeneity

Under the assumption of a temperature independent lifetime τ,[22] an examination of the effect of varying the parameter τ in the TSC Eqs. (1) and (2) leads to some interesting results. The most important one is that while the peak temperature T_m is completely independent of τ for slow traps, it is a function of τ for fast ones. A technique has therefore been recently proposed[16] whereby the correlation of TSC spectra of different samples that have approximately the same trapping structure, but different recombination lifetimes, could

be used to identify the type of trapping kinetics. In analyzing the results of the TSC measurements in Sec. IV, this technique has proved to be very useful.

The importance of considering resistivity inhomogeneity in TSC analysis has been recently discussed in some detail,[10] and it has been demonstrated, in particular, that inhomogeneity is especially critical when studying the properties of closely compensated semiconductors such as the zinc-doped silicon considered here. Since the lifetime of different regions within an inhomogeneous sample would not be generally equal, the TSC spectrum of such a sample would consist, in the simple case of a single type of fast traps, of the superposition of several simple TSC curves which have different peak temperatures T_m, and would therefore substantially deviate from the theoretically predicted TSC curve. Overlooking the effect of inhomogeneity could therefore lead one to conclude the presence of several types of traps or of a continuous trap distribution, whereas in reality only one type of discrete trap is present. Since the shape of the TSC curve and the position of its peak are both independent of τ for slow traps [Eqs. (1) and (2)], no distortion in the TSC curve in an inhomogeneous sample is expected.

C. Trap-filling mechanism

A final effect that, to the best of our knowledge, has not been previously discussed in the present context, and that may be used to determine the type of trapping, is related to the fact that if the illumination intensity is sufficiently strong, such that the quasi-Fermi-level for electrons E_{Fn} (defined by $n = N_c e^{-E_{Fn}/kT}$) where n is the density of free electrons in the conduction band, is several kT above the trap level, a fast trap must be completely filled whereas this will not necessarily be true for a slow one. This happens because a fast trap reaches quasiequilibrium with the conduction band in a time that is small compared with the lifetime τ, i.e. in a fraction of a second, after which the density of trapped electrons will be given by,

$$N_t^- = \frac{N_t^0 n}{n_{t1}} = \frac{N_t n}{n + n_{t1}} = \frac{N_t}{1 + \exp[(E_{Fn} - E_t)/kT]} \sim N_t . \qquad (4)$$

On the other hand, for a slow trap the trap filling time could be very long and, therefore, the illumination might not substantially fill the trap. The equation describing the filling of a slow trap can be derived by an extension of Ryvkin's transient photoconductivity analysis[4] to the case of an arbitrary excitation intensity. The solution of the rate equations in that case could be carried out with n treated as a constant $n \approx G\tau$, where G is the generation rate, to yield for $N_t^-(t)$,

$$N_t^-(t) = (nN_t^0/n_{t1})(1 - e^{-t[\beta_{tn}^0 (n + n_{t1})]}) , \qquad (5)$$

where $n_{t1} = N_c e^{-E_t/kT}$, which shows that if E_{Fn} is above E_t, the slow trap will eventually fill completely as in the case of a fast trap. However, the time constant of trap filling will equal in this case $[\beta_{tn}^0 (n + n_{t1})]^{-1}$, which in real situations might be exceedingly large (hours or days) depending on both the trap depth, the temperature, and the excitation intensity.

The above discussion leads to a method for characterizing the type of trapping by comparing the magnitude of a TSC peak as the intensity, time or temperature of excitation vary, while maintaining $E_{Fn} < E_t$ satisfied. For a fast trap, no effect on the magnitude of the peak should be observed, whereas the amplitude of the TSC peak due to a slow trap should be dependent on the illumination conditions even when the condition $E_{Fn} < E_t$ is satisfied.

III. EVALUATION OF TRAPPING PARAMETERS FROM TSC MEASUREMENTS

In Sec. II the general features of the TSC curves under different illumination and trapping conditions have been introduced. We now present a brief summary and discussion of the most frequently used techniques for deducing the trapping parameters from TSC measurements.

A. Quasi-Fermi-level (Bube's) method

This method, due to Bube,[2] assumes that at the peak temperature T_m, the quasi-Fermi-level E_{Fn} coincides with the trap level E_t. The trap depth can therefore be determined from the relation

$$E_t = kT_m \ln(N_c/n_m) , \qquad (6)$$

where n_m is the free-carrier density at the peak. This formula, however, has been shown to be accurate only for a fast trap which is initially saturated.[5,6] Also, in cases where severe inhomogeneity is present, the application of Bube's formula could produce some error owing to the uncertainty in the true area of the portion of the sample which is emptying, as well as the uncertainty in the peak temperature T_m. It is instructive to note that Bube's formula always overestimates the magnitude of the trap depth.[24] Another noteworthy property of Bube's method is that if reasonable agreement is found between the trap depth as calculated from Eq. (6), which is based on fast retrapping, and that obtained from an independent method which does not depend on the type of trapping kinetics, then this may be taken as an indication that the trap is of the fast type.

B. Heating-rate methods

Two techniques have been proposed for calculating trap depth by monitoring the change in the TSC peak's properties with the heating rate β. The first method involves plotting $\ln(T_m^2/\beta)$ vs $1/T_m$,[12] while the second requires plotting $\ln(\sigma_{max})$ vs $1/T_m$.[5] Both methods have the advantage of being independent of the type of trapping kinetics. A practical difficulty in these methods is the need to be able to vary the heating rate, and to maintain it constant over a fairly wide temperature range. The most serious reported difficulty with these methods, however, is the necessity of having the same degree of initial trap filling between different runs.[3,6] This is particularly difficult to achieve when decayed TSC experiments are required in order to separate several nearby peaks, or in the case of slow traps where the trap filling is sensitive to the excitation conditions (Sec. IIC). It can be shown, however, [Eqs. (2) and (3)] that by maintaining a small trap population ($\eta_0 \leq 0.1$), the plot of $\ln(T_m^2/\beta)$ vs $1/T_m$ becomes practically independent of trap population. On the other hand, the plot that involves σ_{max} is always very sensitive to any variation in the initial trap population and should, therefore, be regarded as less reliable.

C. Methods based on the geometry of the TSC curve

Several authors derived expressions that relate the trap depth to the width of the peak.[3,13,25] These expressions were frequently associated with either fast or slow retrapping, and they made use of the half-width of the peak from either the low- or the high-temperature sides. After investigating all these methods, we believe that the most general, accurate, and useful formula was that due to Dussel and Bube,[6] namely,

$$E_t = 1.41\, kT_m T_L/(T_m - T_L) \quad , \tag{7}$$

where T_L is the half-width temperature below the peak.[26] This equation is valid for both fast and slow retrapping provided that the lifetime is temperature independent, and the trap is weakly populated ($\eta_0 < 0.1$). From practical considerations, however, since the half-width is typically small ($\sim 10\,^\circ$K), any slight uncertainty in the values of T_L or T_m would reflect itself as a large error in the calculated trap depth. The error becomes even greater when the interaction of nearby peaks or inhomogeneity effects are present.

In the initial-rise method,[11] the trap depth is calculated from the slope of the initial linear portion of the TSC curve that results from a plot of $\ln(n)$ vs $1/T$. As was pointed out by Dussel and Bube,[6] this technique is in many cases superior to all other methods of determining the trap depth. It has also been recently shown that the slope of the initial part of the TSC curve remains an accurate measure of the trap depth even in the presence of severe inhomogeneity.[10] The only situations where the accuracy of the method deteriorates are when substantially filled fast traps are present,[6,15] and/or measurements of TSC current far below the peak are hampered by experimental difficulties, such as the low-temperature limit of the system, or a drop in the signal-to-noise ratio. The first problem, however, could be experimentally eliminated by ensuring that in every case the traps are relatively empty.

More recently, a curve-fitting technique has been developed by Cowell and Woods.[22] This approach depends on adjusting the trap parameters until the experimentally measured TSC curve fits the theoretical curve as represented by Eq. (1). The usefulness of this technique, however, is limited to cases when a single well-isolated trap is emptying under first-order kinetics in a homogeneous sample. Provided that the type of trapping can be established by some independent means, the technique could serve to confirm estimates of trapping parameters, and provide a good test of the applicability of the assumed theoretical TSC model.

IV. EXPERIMENTAL PROCEDURE

The main objective was to prepare several homogeneous high-resistivity n-type zinc-doped samples that have the same trapping structure, but different recombination lifetimes. This was achieved by preparing all the samples from the same starting material under carefully controlled conditions. The dark current, steady-state photocurrent, and ordinary as well as decayed thermally stimulated currents were then measured as a function of temperature on each sample.

In order to minimize the concentration of accidentally occurring traps with respect to that of zinc, it was decided to use float-zone silicon containing a donor impurity concentrating N_d close to the maximum solid solubility of Zn in Si. In light of these considerations, Lopex silicon, containing approximately 1.2×10^{16} cm^{-3} of As, was purchased from Texas Instruments Inc. The as-received material was in the form of 1-mm-thick circular disks cut parallel to the (111) crystal plane. The resistivity was specified by Tl to be in the range 0.3–0.5 Ωcm, with a maximum radial variation of 10% within a slice. Lifetime was claimed to be less than 10 μsec.

A standard closed-ampoule single-temperature diffusion technique was used on lapped, precleaned, and etched slices. The zinc was 99.999% pure. Diffusion times were not less than four days and were terminated by rapid quenching of the ampoule

in water. The samples were then cleaned, after which Ohmic contacts were applied to the large-area faces using the electroless plating of nickel. Finally, the samples were diced into rectangular pieces having dimensions of approximately $4\times3\times0.3$ mm^3 in order to minimize inhomogeneity effects.

The variation of sample current with temperature was measured using a Keithley 610C electrometer connected in series with the sample, a relatively small load resistor, and a 6-V battery. The TSC currents were continuously recorded on an x-y recorder. Temperature control was achieved by mounting the sample in an Oxford Instruments CF104B cryostat, which was associated with a precision temperature indicator and controller. Linear heating rates in the range 3–12 °K/min in the temperature range 77–150 °K, and 2–6 °K/min in the range 150–250 °K were achieved by controlling the nitrogen-flow rate and the heater power of the cryostat. The voltage across the cryostat's temperature sensor element was connected to the x-y recorder in order to provide the horizontal display.

Illumination was achieved by means of a tungsten filament, quartz halogen lamp. Band-gap radiation was obtained by using narrow-band Baird Atomic optical filters with pass bands centered in the range of 1.08–1.12 μm. White light was frequently tried with essentially the same results. Variations of illumination intensity were achieved by a set of neutral density filters, which allowed attenuation of up to 10 decades of intensity.

Two types of TSC measurements were carried out: ordinary TSC, which consisted of illuminating the sample at 77 °K, leaving it in the dark for 5 min and then raising the temperature at a linear rate; and decayed TSC which involved heating the sample to a prescribed decay temperature, rapidly cooling the sample to 77 °K, and subsequently heating again without further excitation.

V. RESULTS

Several slices were diffused with zinc at temperatures in the range 1050–1150 °C. A comparison of the room-temperature resistivity of the individual samples obtained after dicing a slice was used as an indication of the diffusion uniformity. The four samples listed in Table I were those that turned out to be high-resistivity n type and homogeneous to within a factor of 2 on the basis of the above method of evaluation. Note that, for the purpose of comparison, one of the samples was produced from Czochralski-grown silicon.

The contacts of all the samples remained essentially ohmic at all temperatures, except the near-intrinsic sample 4, which exhibited appreciable nonlinearity in the current-voltage characteristic. The dark current of all four samples was found to decrease as expected with temperature, with an activation energy of approximately 0.5 eV, which corresponds to the approximate location of the upper zinc level E_2.[18]

TABLE I. Zinc-doped silicon samples

Sample No.[a]	T (°C)	Type	Average ρ ($10^3\ \Omega$ cm)	N_z (10^{15} cm^{-3})
2	1080	n	4	6.1
3	1100	n	20	7.2
4	1100	n	150	9.9
7[b]	1100	n	4	6.1

[a]The sample numbers are the same as those used in Ref. 18.

[b]Starting material was Czochralski silicon.

Since in our samples, holes are understood to be detained at the doubly negatively charged zinc ions leaving only electrons to contribute to the TSC current, and because the lifetime is controlled by the temperature invariant large density of the singly negatively charged zinc ions $N_z^-[\tau=(\beta_{zn}N_z^-)^{-1}]$, and is therefore expected to be temperature independent,[18,27] the TSC model of the samples was anticipated to ideally resemble the simple one which was considered in Sec. II. We found, however, that the TSC spectra of all samples exhibited considerable complexity, and that the shapes of the TSC peaks deviated sharply from those predicted by Eq. (1) in most cases. We carried out the TSC experiment with varying heating rates and illumination intensities and performed several decayed TSC experiments in each case. In the analysis of our measurements, we applied as many techniques as appropriate. In the light of the preceding discussion a weak trap population ($\eta_0<0.1$) was considered desirable for all techniques, except Bube's which required the highest possible illumination intensity ($\eta_0\sim1$).

Table II shows a summary of the TSC results for the various samples. The error limits indicated in the table were based on the variations in results among no less than five to ten identical runs, and take into consideration the various sources of uncertainty. These include the uncertainties in the temperatures T_m and T_L, the magnitude and temperature dependence of mobility, the effective sample dimensions, and, whenever possible, an estimate of the error due to inhomogeneity interference. As can be seen from the table, the initial-rise and Bube's method yield, in general, the least scatter. Below, the results of the individual samples are presented and discussed in some detail. This is followed by

TABLE II. Summary of trapping levels detected in the zinc-compensated silicon samples by the various TSC techniques.

Sample No.	Heating rate (° K/min)	T_m[a] (° K)	E Bube (eV)	E Initial rise (eV)	E Heating rate (eV)	E Half-width (eV)	Type of trapping
3	11	98	0.2±0.01	0.19±0.01	•••	0.15±0.03	Fast
	5.5	208	0.42±0.01	0.41±0.01	0.4±0.04	0.45±0.04	Fast
4	11	98	0.21±0.01	0.17±0.02	•••	0.12±0.02	Fast
2,7	11	90	0.12±0.01	0.1±0.02	0.1±0.02	0.11±0.02	Fast
	11	105±5	0.15±0.02	0.14±0.02	•••	•••	Fast
	11	125±3	0.21±0.02	0.21±0.01	•••	•••	Fast
	5.5	208±1	0.39±0.02	0.36±0.02	0.35±0.06	0.28±0.06	Slow

[a]The quoted values of T_m correspond to the heating rates in the preceding column.

a discussion of how the results of the different samples can be correlated to each other, yielding a consistent model.

A. Results of the higher resistivity samples 3 and 4

Figure 1 shows the TSC spectra of sample 3, recorded after different illumination intensities at 77 °K. As indicated on the figure, the illumination intensity is expressed in terms of the location of the quasi Fermi level of electrons under illumination, E_{Fn}. The common features of all the TSC curves are the existence of a continuous distorted spectrum that extends over the temperature range 77–140 °K and comprises a TSC peak at 98 °K, followed by another fairly well defined peak at 208 °K. Note that reducing the illumination intensity within the indicated limits causes no effect whatsoever, either on the magnitude and shape of the 208 °K peak or on its location. Only in the case when very weak illumination (E_{Fn} ~ 0.42 eV) was used at T = 160 °K, could the amplitude of this peak be reduced to about $\frac{1}{10}$ of its value. In that case, the peak location was found to shift upward by about 6 °K.

In order to determine whether the results are influenced by inhomogeneity or are actually due to multilevel traps, we undertook several decayed TSC measurements. Figure 2 shows typical decay results which were recorded following illumination of the sample at 77 °K by an intermediate intensity (E_{Fn} ~ 0.16 eV). It is evident that decay causes the 98 °K peak to continuously shift up to 140 °K. Repeating the TSC measurements, but with illumination temperatures varying in the range 77–140 °K and no decay, resulted in similar plots. Since all the initial rise lines in Fig. 2 have approximately the same slope, this may be taken as an indication that the whole spectrum up to 140 °K belongs to the same trap, and that sample inhomogeneity was responsible for the observed distortion of the peak.[28] Moreover, we were able to infer that the trap is of the fast type because the TSC peak due to a slow trap is independent of sample inhomogeneity (Sec. IIB). Further evidence in support of the argument that the trap is of the fast type is provided by the good agreement between the trap depth calculated from Bube's method (assuming the presence of the principal peak of 98 °K) and the initial-rise method.

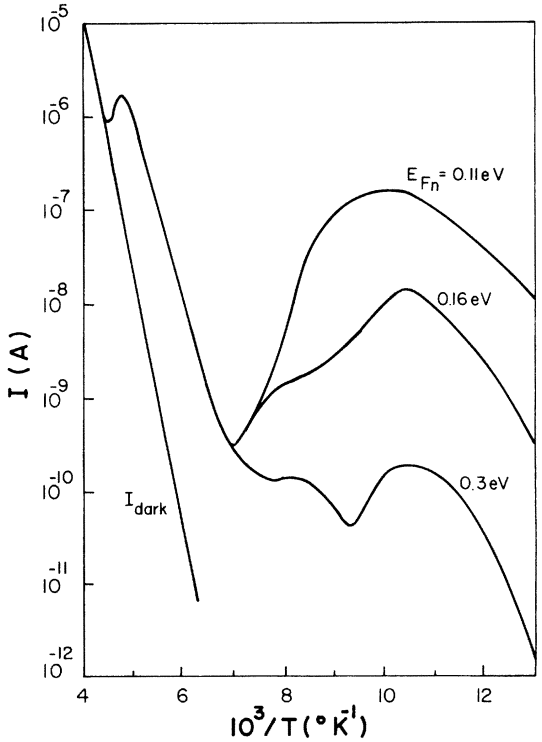

FIG. 1. TSC measurements of sample 3, following 5-min illumination at 77 °K with various intensities. Numbers on the curves indicate the location of the quasi-Fermi-level of electrons E_{Fn} under excitation.

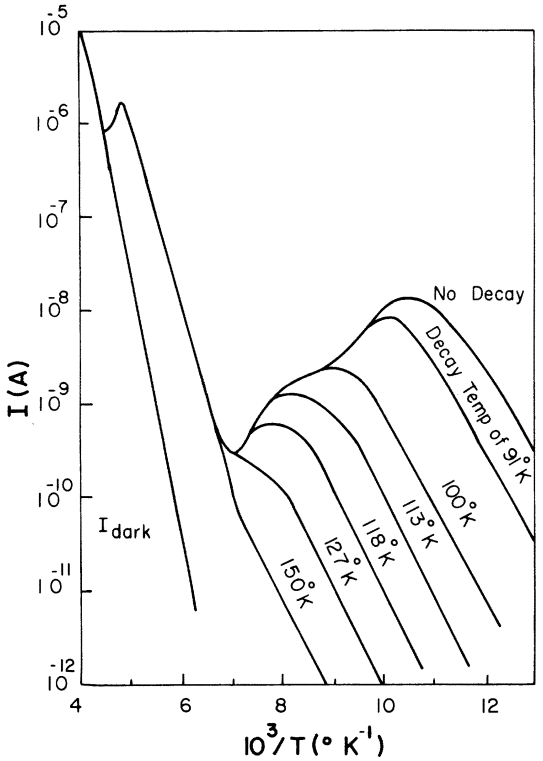

FIG. 2. Decayed TSC measurements in sample 3, following illumination at 77 °K that placed the quasi-Fermi-level E_{Fn} at 0.16 eV.

The emphasis of the peak at 120 °K relative to the main one at 98 °K which occurs at the lower illumination intensity can also be given a plausible explanation. When the illumination is weak and the average quasi-Fermi-level E_{Fn} is below the trap level ($E_{Fn} \sim 0.3$ eV), the degree of trap filling owing to excitation in each portion of the sample would be dependent on the local excess free-carrier density, which in turn depends on the lifetime in this region. Therefore, the reduction of the amplitude of the TSC spectrum would be greater in those parts of the sample with the shorter lifetime and, consequently, having a lower peak temperature T_m. The fortituous distribution of inhomogeneity in this sample allowed the addition of the TSC spectra of its individual regions to yield a double peak.[10]

It is interesting to note that without doing decay or taking the inhomogeneity effect into consideration, the wide TSC spectrum would be thought of as being due to the overlapping of the spectra of several traps or as being due to a continuous trap distribution. Application of Bube's formula, for instance, could point to the existence of a continuous trap distribution in the range of 0.2 to 0.3 eV from the conduction band, or, at least, to the existence of several discrete trap levels in that range.

The decay had no noticeable effect on the 208 °K peak, which is found to be reasonably well defined. This could be interpreted as being the result of either the trap being a slow one, and therefore inhomogeneity was not important, or of the trap being fast and inhomogeneity interference having no noticeable effect because of the relatively high temperature.[10] We have some evidence that the trap is fast. First, is the good agreement between Bube's and all other methods. Also the 6-°K shift in the peak that occurred with wide variations of illumination intensity is a property of a fast trap and agrees in order of magnitude with the shift predicted by Eq. (3). Therefore, there is strong evidence that this is the same fast trap for whose existence we had found evidence from photodecay measurements.[18] The location and density of this trap have been reported to be, respectively, 0.4 eV and $\sim 10^{13}$ cm^{-3},[18] and its electron-capture cross section has been estimated[29] to equal approximately 10^{-16} cm^2.

The TSC results of the near-intrinsic sample 4 which are plotted in Fig. 3 exhibit one main peak at 98 °K, and a continuous spectrum up to about 120 °K. In the range 120–200 °K, the TSC current was comparable to the dark current of this sample, making it difficult to accurately analyze this portion. Decayed TSC measurements in the range 77–120 °K exhibited approximately parallel straight lines, indicating that a single trap was emptying in that range. By the same argument as used above, it could be concluded that this trap is of

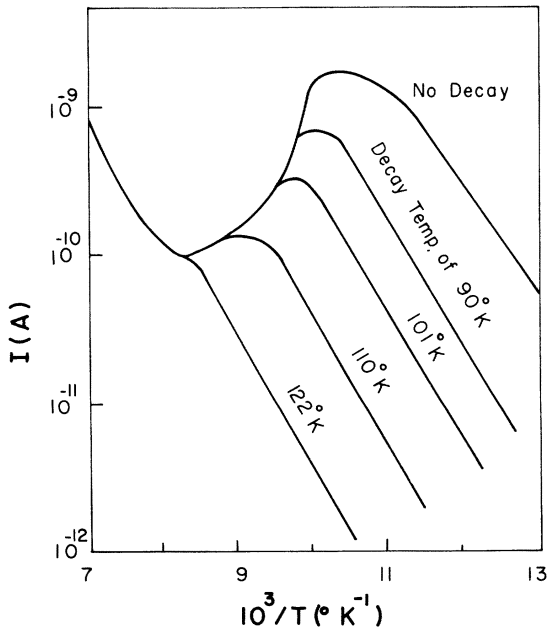

FIG. 3. TSC measurements of sample 4.

the fast type. The discrepancy between Bube's and initial-rise methods is probably because of the somewhat non-Ohmic behavior of this sample's contacts.

B. Results of the lower-resistivity samples 2 and 7

The results of samples 2 and 7, which have the same resistivity but were made from different starting materials, were essentially similar. Figure 4 shows the result of several TSC runs for sample 7, recorded after different illumination intensities at 77 °K. As may be seen, all curves have the same features, namely, one principal peak at 90 °K, a continuous spectrum up to ~ 140 °K, and a shoulder in the temperature range 190–220 °K. This shoulder yields, after subtracting the dark current, a fairly well defined peak at 208 °K.

The decayed TSC results, which are plotted in Fig. 5 show, in a manner similar to the high-resistivity group, that the position of the peak temperature was continuously shifting from 90–140 °K, depending on the decay temperature. In the lower-resistivity samples, however, the decay lines are not all parallel, which points to the presence of more than one type of trap that empties in that temperature range. Using the parallelism of the decay lines as a criterion for separating the contribution of each trap, we conclude that this wide spectrum consists of the contributions of up to three traps, which are associated with the principal peak at 90 °K, and the two minor peaks at approximately 105 and 125 °K. Because of the severe trapping interaction, the application of the heating rate and half-width methods to the intermediate peaks at 105 and 125 °K were not deemed reliable, and accordingly were not included in Table II.

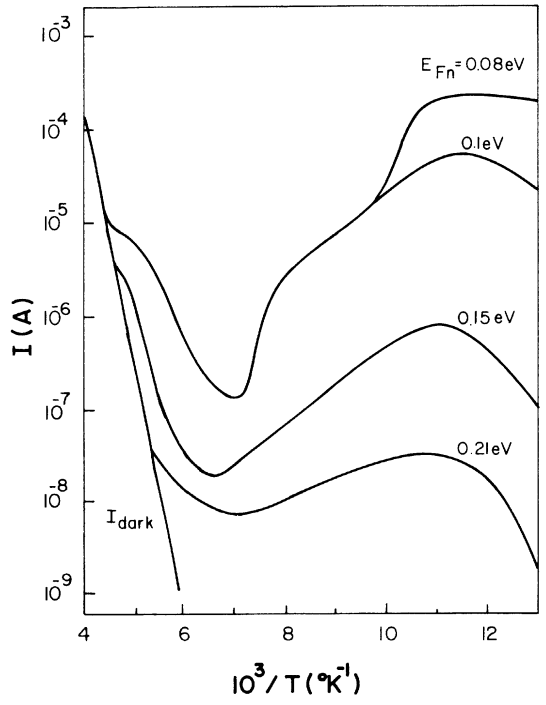

FIG. 4. TSC measurements of sample 7 following various illumination intensities at 77 °K.

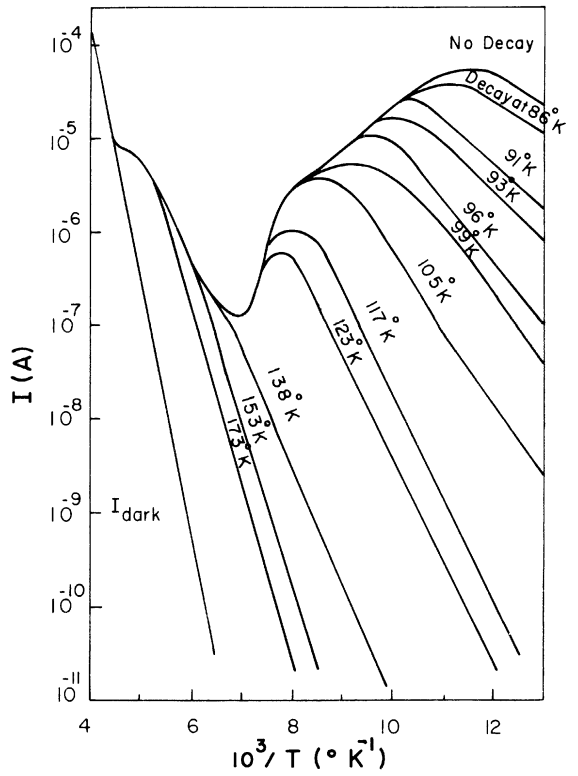

FIG. 5. Decayed TSC measurements in sample 7, following illumination at 77 °K that placed the quasi-Fermi-level E_{Fn} at 0.1 eV.

The trapping mechanism corresponding to the peak at 90 °K appears to be of the fast type. This is based on the reasonable agreement between Bube's and the other methods, as well as on the ~4-°K shift in the position of the peak that resulted from a wide variation of illumination intensity, in rough agreement with Eq. (3). Because of the relatively large uncertainty in the estimated depth and location of the TSC peak at 105 and 125 °K, the criterion which is used for determining the type of trapping for the 90 °K peak was not very reliable. However, the wide spread of the TSC spectra belonging to the two peaks at 105 and 125 °K may be taken as an indication that both these traps are of the fast type [Sec. II B)].

Meanwhile, the 208-°K trap definitely appears to be emptying under a slow retrapping mechanism. Aside from the relatively high value of E_t that Bube's formula yields, which points to a slow

trap, the trap filling mechanism could be the deciding factor here. As may be seen from Fig. 4, illumination intensities that caused E_{Fn} to be in the range 0.15 − 0.21 eV, a location far above the level of the trap, still left the trap substantially empty. A straightforward application of the reasoning presented in Sec. (II C) would leave no doubt about the type of this trap. Having established the slow nature of this trap, Eq. (2) may be used, yielding an approximate value of 10^{-20} cm^2 for the electron-capture cross section of this trap.

C. Correlation of the results of different samples

A comparison of the measured photocurrents under identical illumination intensities of the different samples was used in order to determine the ratio of their lifetimes. For that purpose, the illumination intensity was adjusted such that the photocurrents were approximately equal to the TSC currents. Although the measured photocurrents were found to be somewhat dependent on both the illumination and thermal cycle of the sample, by averaging the measurements of several runs we were able to infer some useful results. The respective lifetimes of samples 4, 3, and 7 were approximately in the ratio of 1: 5: 100 at 200 °K, and 1: 10: 10^4 at 100 °K. Although these values show that the lifetimes of the lower-resistivity samples were the longest, as is theoretically predicted, the lifetimes did not simply correlate with the values obtained from $\tau = (\beta_{zn}^- N_z^-)^{-1}$ which yields a temperature-independent-lifetime ratio of 1 : 3 : 10.[18] The reason for the discrepancy could be interpreted as being due to inhomogeneity, which is very significant in closely compensated samples.[10]

Correlating the TSC results of all samples can help in further clarifying the picture and verifying our conclusions. The most obvious observation was that the TSC currents of the different samples were approximately proportional to their lifetimes, in agreement with the TSC theory for both fast and slow traps. Table II and the preceding analysis indicate that five types of traps are active in our samples, with approximate locations from the edge of the conduction band of 0.1 ± 0.02, 0.14 ± 0.02, 0.19 ± 0.02, 0.41 ± 0.01, and 0.36 ± 0.02 eV. All traps empty under fast kinetics except the latter which empties under slow kinetics. The above conclusions, as will be seen, were substantiated by considerable evidence, besides that already presented.

The fact that both the 0.1- and 0.14-eV traps were only observed in samples 2 and 7 and not in the other samples is not difficult to explain in the light of the discussion given in Sec. (II B) about the lifetime dependence of the position of the TSC peak of a fast trap. Those traps were not observed in samples 3 and 4 because they would empty in these samples at temperatures in the range of 45–60 °K, which is well below the lower limit of our measuring system, namely 77 °K. Another case is the 0.19-eV trap which has been shown to correspond to TSC peaks at 97 and 125 °K in samples 3 and 7, respectively. The spacing between the peaks is in approximate agreement with the 40 °K which would be expected based on the lifetime ratios of the two samples. Although the 10-°K separation in the peak which had been predicted for samples 3 and 4 was not observed, the fact that the contribution of this trap extends in sample 3 up to 140 °K, and in sample 4 only up to ~120 °K is in qualitative agreement with the theory.

One of the most interesting findings in this work is that the 208-°K peak, which was observed simultaneously in both samples 3 and 7 corresponds to two entirely different traps. The reason that the 0.41-eV trap was only observed in sample 3, while the 0.36-eV trap was only detected in sample 7, can be explained in the light of the TSC theory presented in Sec. II. The 0.41-eV trap, owing to its fast nature, would have a TSC peak in sample 7 which is about 20 °K higher than that in sample 3, and would therefore be obscured in sample 7 at such a high temperature by the already relatively large dark current of this sample. On the other hand, despite the fact that the 0.36-eV slow trap would have a TSC peak temperature independent of sample, the failure to detect this trap in sample 3 could be due to one of two reasons. The first comes from the proportional relationship between the amplitude of the peak and the lifetime, that causes the peak amplitude in sample 3 to be approximately an order of magnitude smaller than in sample 7. The second reason is the difficulty in appreciably filling this trap in sample 3 at 77 °K. Since the highest steady-state free-electron density under illumination in sample 3 was less than those attained in sample 7, the increase in the trap-filling-time constant in sample 3 could have made the filling of this trap more difficult.

A comparison with the results of other workers is hampered by the fact that the published data on TSC measurements in zinc-compensated silicon are brief and scattered.[30–33] Based on the existing knowledge about trapping in silicon, it could be that the traps we located at 0.1, 0.19, 0.36, and 0.41 eV are, respectively, due to the interstitial zinc,[34] the A center, the double-acceptor silicon divacancy, and the E center.[35]

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