

A NEW MODEL OF NEGATIVE PHOTOCURRENT⁺

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Abstract—A one-deep-energy-level impurity, space-charge neutral and steady-state model is proposed and verified in *n*-type silicon N^+IN^+ diode samples which are overcompensated but not inverted by gold acceptors in the slightly *n*-type *I*-region. The model is as follows. If the photoionization rate of trapped holes at the impurity center is greater than electrons, then an extrinsic monochromatic light will increase the trapped electron concentration. To maintain quasi-neutrality and a constant steady-state trapped electron concentration (equal to the concentration of the shallow level donor), the injected electron concentration into the compensated *n*-type *I*-region must decrease. Thus, the electron or the total conduction current must also decrease since the hole concentration is very low in the presence of a large sweep-out electric field and the hole conduction current may be neglected. This model has successfully predicted the observed large negative photocurrent (NPC) which is as much as 2/3 of the dark current, the large intrinsic optical gain (about 50) and the sublinearity in dark current.

I. INTRODUCTION

Negative photoconductivity or photocurrent (NPC) have been reported in many amorphous materials.^{1,2} Well defined NPC was first observed by Stockmann^{3,4} in electron irradiated Ge. There have been renewed interests on this effect with experimental observations in *n*-type semiconductors which are overcompensated by some deep-level impurities such as gold-doped Ge,⁵ cobalt-doped Si⁶ and gold-doped Si.⁷ The interpretation of the experimental results have been very qualitative and based on Stockmann's two-level impurity model.⁴ In this model, very specialized conditions on the thermal capture cross-sections of minority carriers are required.³ Because of the small magnitude observed, the NPC effect was thought to originate

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from a different mechanism than that which gives rise to large intrinsic photoconduction and optical gain.

This paper shows that the observed extrinsic NPC, high intrinsic optical gain and its associated sublinear dark current can all be completely accounted for by a deep one-level impurity model in an applied electric field. In contrast to Stockmann's equilibrium model, the new steady-state model shows that NPC ceases when the applied electric field is reduced below a threshold due to the presence of sufficiently large number of minority carriers.

II. PHYSICS OF THE MODEL

Consider a N^+IN^+ diode structure under an applied voltage V whose energy band diagram is shown in Fig. 1. The shallow-level donor in the I-region (with concentration N_D) is overcompensated by a deep-level acceptor impurity ($N_{TT} > N_D \sim 10^{15}/\text{cm}^3$). The compensation is insufficient to invert the I-region so that it is still slightly n -type ($N \gg P$). Thus, the conduction is dominated by electrons drifting from the left N^+ region through the I-region to the right N^+ region. Below about 10^5 V/cm electric field when the space charge dE/dx is unimportant, electric neutrality is maintained over the entire I-region except the small end region near the cathode (the N^+ region on the left) which can be neglected. Thus, almost all the excess electrons from the shallow-level donors are trapped at the deep-level acceptor, i. e. the trapped electron concentration N_T is approximately equal to the shallow donor concentration N_D . As a consequence, the electron concentration in the I-region is very small: $N \ll N_T \simeq N_D$. One of the most important point of this new model is that the condition of constant trapped electron concentration will persist under illumination if $N_D > 10^{15}/\text{cm}^3$ since for practical light intensities ($\phi < 10^{16}$ photons/ cm^2 -sec.) the photoelectron concentration will satisfy the inequality $N \ll N_D \simeq N_T$.

When the sample is exposed to an extrinsic monochromatic light, trapped electrons (concentration N_T no./ cm^3) and holes (concentration $P_T = N_{TT} - N_T$) are released to the conduction and valence bands. If the photoionization rate of trapped holes, $e_p^0 P_T$ shown in Fig. 1, is greater than that of trapped electrons, $e_n^0 N_T$ shown in Fig. 1, then the trapped electron concentration would increase which is not possible due to charge neutrality which gave $N_T = N_D = \text{constant}$. Thus, the increase of the rate due to $e_p^0 P_T$ over $e_n^0 N_T$ must be balanced by a decrease of the thermal capture rate of electrons, $c_n^0 N P_T$ shown in Fig. 1. This would decrease the electron concentration in the I-region, N , by reduced injection of electrons from the left N^+ region over the small potential barrier maximum. Decreasing N then gives a negative photocurrent.

The neglected hole (minority) contribution to the current, which is positive unde illumination since P increases with illumination, is small due to the presence of a large electric field which sweeps out the holes. However, holes and the space charge due to the photoelectrons and photoholes will set the lower limit on the applied electric field below which the NPC will cease and the photocurrent becomes positive.

III. MATHEMATICAL SOLUTION

The solution can be readily obtained from the physical model just discussed and the simple solution neglecting hole contributions will be given first which is valid in high electric fields.

Electrical neutrality in the I-region gives $0 = P - N + N_D - N_T \simeq N_D - N_T$ when the total deep level concentration, N_{TT} , is greater than the shallow level donor concentration, N_D , and when $N_D > 10^{15}/\text{cm}^3$. The trapped electron concentration can be obtained from the steady-state balance of the six rate processes shown in Fig. 1, giving $c_n^t N P_T - (e_n^t + e_n^o) N_T = c_p^t P N_T - (e_p^t + e_p^o) P_T$ so that

$$c_n^t N = (N_T/P_T)(e_n^t + e_n^o + c_p^t P) - (e_p^t + e_p^o) \quad (1)$$

$$\simeq [N_D/(N_{TT} - N_D)](e_n^t + e_n^o) - (e_p^t + e_p^o) \quad (1A)$$

where the approximation in (1A) made use of $P \ll N \ll N_D \simeq N_T = N_{TT} - P_T$. The photoelectron concentration in the I-region, ΔN , is then given by

$$c_n^t \Delta N = [N_D/(N_{TT} - N_D)]e_n^o - e_p^o \quad (2)$$

NPC is obtained if $\Delta N < 0$ or when $e_p^o/e_n^o > [N_D/(N_{TT} - N_D)]$. This condition on the ratio of the minority to majority carrier photoionization rates is possible for over-compensated but still *n*-type I-region where $N_{TT} > N_D$ and for the gold acceptor level located at 545 meV below the Si conduction band edge which has $e_p^o/e_n^o < 1$ in the extrinsic range of $\hbar\omega > 670$ meV.⁸ However, the inequality for achieving NPC can still be satisfied even if $e_p^o/e_n^o < 1$ provided that $N_{TT} \gg N_D$.

In the next section, (2) is tested experimentally and found to give excellent results.

To establish the low electric field limit for NPC, the positive hole contributions must be included in the solution. In addition, the photo space charge must also be included if the threshold applied field is very low. We shall only consider the high threshold field in this paper.

The importance of the hole contributions is evident in (1) since the hole capture term, $c_p^t P$, when included in (2) will reduce the negative photoelectron concentration. The hole concentration can be obtained from the steady-state rate balance between hole capture at the deep level center and the sweep out of holes by the electric field across the I-region, giving

$$P/t_p = (e_p^t + e_p^o)(N_{TT} - N_T) - c_p P N_T \quad (3)$$

where $t_p = L/\mu_p E$ is the hole transit time across the I-region of length L and E is the magnitude of the electric field.

The hole and electron concentrations in the charge neutrality condition, $\rho = q(P - N + N_D - N_T) = 0$, may still be neglected as long as $N_{TT} > N_D \simeq N_T \gg N \gg P$ which is valid in practice as we have just discussed. Using $N_T \simeq N_D$, the hole concentration from (3) is given by

$$c_p^t P = (e_p^t + e_p^o)[(N_{TT}/N_D) - 1]/[1 + (\tau_p/t_p)] \quad (4)$$

and the electron concentration from (1) and (4) is then

$$c_n N = [N_D / (N_{T^+} - N_D)] [(e_n^+ + e_n^-) - \{(\tau_p / t_p) / [1 + (\tau_p / t_p)]\} (e_p^+ + e_p^-)] \quad (5)$$

where $\tau_p = 1/c_p^+ N_{T^+} = 1/c_p^+ N_D$ is the hole lifetime in the I-region. These results are also valid at thermal equilibrium, $E = 0$, since (3), the continuity equation of hole, is still valid. They show that the thermal equilibrium electron and hole concentrations would increase with illumination, $e_n^+ = \sigma_n^+ \Phi$ and $e_p^+ = \sigma_p^+ \Phi$, and no negative photoeffect would be observed.

The minimum electric field required for NPC can be obtained from the photo-current inequality $\Delta j = q(\mu_n \Delta n + \mu_p \Delta p) E + q(\mu_n N + \mu_p P) \Delta E < 0$ where E , P and N are the steady-state dark values and ΔE must be obtained from $\epsilon d\Delta E/dx = \Delta \rho = q(\Delta P - \Delta N - \Delta N_{T^+})$ due to unneutralized photo space charge. As a first approximation, we shall neglect the term due to ΔE . This is valid if the threshold field is high or when the minority carrier transit time is much smaller than its lifetime, $t_p / \tau_p \ll 1$. In practice, we shall see that our experimental sample satisfies this condition.

Making use of (4) and (5), and the 'high field' threshold condition $\mu_n \Delta n + \mu_p \Delta P \leq 0$, the threshold electric field for the onset of NPC is then

$$\tau_p / t_p = \mu_p E / L c_p^+ N_D \geq \{1 + (e_p^+ / e_n^+) (\mu_p / \mu_n) (c_n^+ / c_p^+) [(N_{T^+} / N_D) - 1]\} / \{ (e_p^+ / e_n^+) [(N_{T^+} / N_D) - 1] - 1 \} \quad (6)$$

The second term in the numerator comes from the positive photohole current which is small compared with 1 at the gold acceptor level in Si since $c_n^+ \ll c_p^+$ for this case. A simpler analysis of the threshold condition can be made for the case of small hole photo current since we would then require $\Delta n < 0$ only. From the steady-state balance of the six processes indicated in Fig. 1, we have $c_n^+ P_{T^+} \Delta n =$

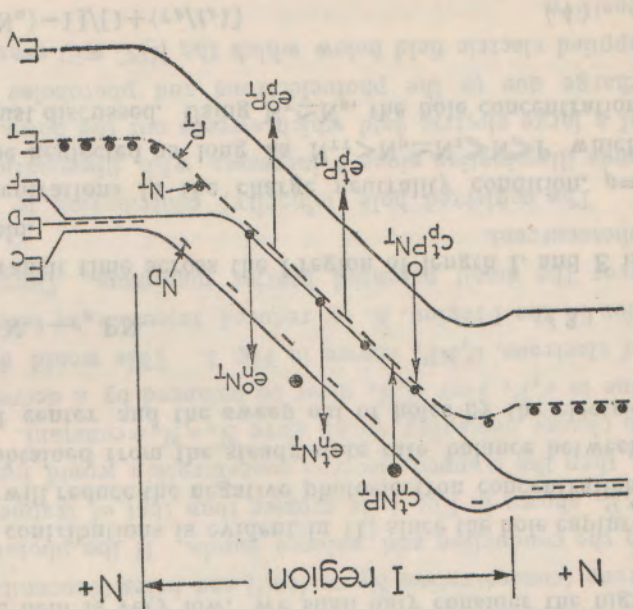


Fig. 1. The energy band diagram of an N+IN+ diode structure.

The I-region is doped with a shallow level donor of concentration N_D and over-compensated with a deep level acceptor with concentration N_{T^+} and energy level E_{T^+} . N_{T^+} and $P_{T^+} = N_{T^+} - N_{T^+}$ are the trapped electron and hole concentrations at the deep acceptor level. The six vertical arrows indicate the four thermal capture and emission processes and the two photoionization processes of electrons and holes under extrinsic illumination. The rates of the six processes are shown next to the arrows as $c_n^+ N_{T^+}$, etc.

$e_n^0 N_T + c_p^t N_T \Delta P - e_p^0 P_T < 0$. Thus, $c_p^t N_T \Delta P < e_p^0 P_T - e_n^0 N_T$ which states that for NPC, the thermal capture rate of photoholes must be smaller than the photogeneration rate of holes over electrons. This can be reduced into a slightly different form using (3) to give $\Delta(P/t_p) > e_n^0 N_T$ which states that for NPC, the drift rate of photoholes must be larger than the photoelectron generation rate.

The threshold condition of the applied voltage for NPC in this simplified case can be obtained from either one of the two inequalities just obtained by eliminating P from (3). It is given by

$$[t_p^{-1}/(\tau_p^{-1} + t_p^{-1})]e_p^0 P_T > e_n^0 N_T \quad (6A)$$

which is identical to the complete form given by (6) with the photohole current term (second term in the numerator) deleted. It also reduces to the condition following (2) if $t_p \ll \tau_p$, that is, the hole contribution is completely neglected at high fields. The result given by (6A) is intuitively simple: it states that when hole contribution is important, NPC can occur only when the photogeneration rate of holes, $e_p^0 P_T$, reduced by the probability of hole drift relative to thermal hole capture $[t_p^{-1}/(\tau_p^{-1} + t_p^{-1})]$, must be greater than the photogeneration rate of electrons, $e_n^0 N_T$.

Since the minimum or threshold electric field given by (6) is quite low, the NPC effect could be mistaken as a thermal equilibrium process. A numerical estimate can be made for the gold acceptor in Si where $c_n^t/c_p^t = 1.65 \times 10^{-9} + 1.15 \times 10^{-7} = 0.014^9$ and $e_p^0/e_n^0 \simeq 10$. Let $N_{TT}(\text{Au}) = 2N_D = 2 \times 10^{16}/\text{cm}^3$ and $\mu_p/\mu_n = 330/1000$. Then, we have from (6) $\tau_p/t_p = \mu_p E/Lc_p^t N_D > [N_D/(N_{TT} - N_D)](e_n^0/e_p^0) \simeq 0.1$ so that $E(\text{V/cm}) > 40L(\mu\text{M})$. This shows that NPC can be expected at rather low electric fields. For example, let $L = 25 \mu\text{M}$, then $E \simeq 1000 \text{ V/cm}$ and $V = EL = 2.5 \text{ volts}$. Observed threshold voltages are in the range of 0.5 volt for samples of 5 to 10 μM length. In this estimate, τ_p/t_p is less than unity so that the photo space charge must be considered in the analysis.

The high field space charge reduction of the NPC can be estimated from the approximation $\epsilon dE/dx \simeq -\epsilon E/L \simeq \epsilon V^2/L = q(P - N + N_D - N_T) \simeq q(N_D - N_T)$. This shows that N_D in (4) and (5) is to be replaced by $N_D + E/qL$. Thus, an increase in space charge or electric field would reduce the total negative ΔN . However, for $N_D = 10^{16}/\text{cm}^3$, space charge effect becomes important only when $\epsilon E/qL \simeq N_D$ or $E = 4 \times 10^6 \text{ V/cm}$ for $L = 25 \mu\text{M}$. Thus, there is a wide range of applied voltage (10 to 10^4 V for this example) where NPC appears and space charge effect due to high electric field can be neglected.

The negative photocurrent due to the gold donor level ($E_v + 345 \text{ mV}$) in Si predicted by the Stockmann's two-level model can be shown to be negligibly small compared with the contribution from the acceptor level just presented. To estimate this contribution, we note that most of the gold donors are in the neutral state in the I-region and its concentration is $N_{TT} - N_D$. The recombination rate at the donor level is then limited by hole capture whose rate is $c_{p0}^t P(N_{TT} - N_D)$. This must be added to the hole capture term at the acceptor level, $c_p^t P N_T$, in (3) and would increase this term by a factor $(c_{p0}^t/c_p^t)(N_{TT} - N_D)/N_D \simeq (c_{p0}^t/c_p^t) = 2.4 \times 10^{-8}/1.15 \times 10^{-7}$

=0.2. The reduction of the electron concentration due to recombination at the gold donor level (Stockmann's effect) is also negligible since the electron capture rate into the gold acceptor level is considerably larger than into the unoccupied donor level. This ratio is $c_n^t N(N_{TT} - N_D) / (c_{n-1}^t N N_{Au+}) = c_n^t N(N_{TT} - N_D) / c_{n-1}^t N(c_{p0}^t P + e_{n0}) / (c_{n-1}^t N + e_{p-1}) \simeq (c_n^t / c_{n-1}^t) (c_{n-1}^t N + e_{p-1}) / c_{p0}^t P \simeq 10^5$ using the numerical values listed in references 8-10.

IV. EXPERIMENTAL RESULTS

This section presents some earlier experimental verification of the model. A more detailed comparison between theory and experimental, including a detailed analysis of the threshold condition is presented elsewhere.¹¹

Experimental verifications of the new model has been made on gold diffused silicon N⁺IN⁺ diode structures with the following parameters: $N_D = 10^{15}/\text{cm}^3$, $N_{TT}(\text{Au}) = 2$ to $5 \times 10^{15}/\text{cm}^3$, $L = 12 \mu\text{M}$, N⁺ layer thickness = $5 \mu\text{M}$ and area = 0.0045 cm^2 . A comparison of the theory and experiment on the spectral response of the photocurrent is shown in Fig. 2 both in the extrinsic NPC range, labeled (-), and

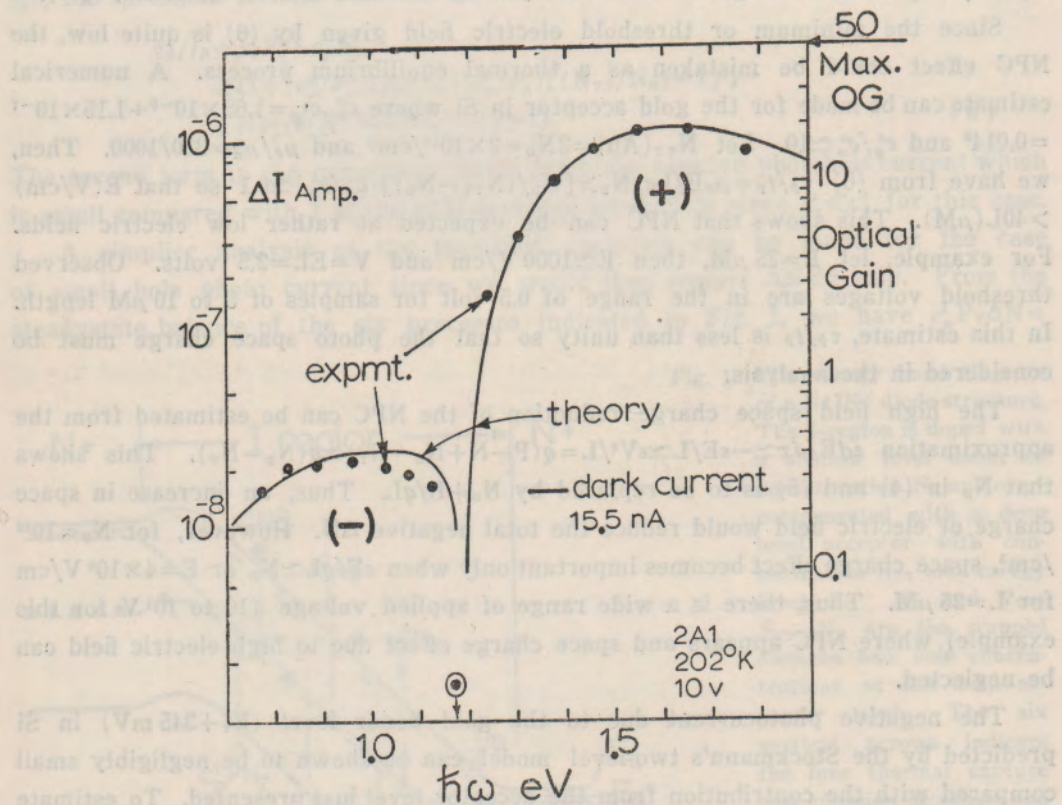


Fig. 2. Comparison of theory with experimental photocurrent spectra taken on a gold doped silicon N⁺IN⁺ diode at 202°K and 10 volts bias. The theory is calculated from (4) and (5) using the data given in references 8, 9 and 10. (-) is the negative extrinsic photocurrent region while (+) is the positive intrinsic photocurrent region.

the positive intrinsic photocurrent range, labeled (+). The theory of the intrinsic range is worked out and presented elsewhere.¹¹ The dark current at the 202°K sample temperature is 15.5 nA while the negative photocurrent peaks at about 10 nA. The scale on the left gives the optical gain, showing a value of 20 at the peak which is both predicted and observed in this sample. The maximum intrinsic internal optical gain is about 50 and the reduction to 20 in this sample is due to the absorption in the top N⁺ layer of 5 μM thickness.

The theory is also tested by comparison with the room temperature pulsed data of Barrett and Gerhard⁷ in Fig. 3. The vertical scale here is shifted to match the theory with experiments since the device geometry and impurity concentrations are not accurately known. The general agreement is again good.

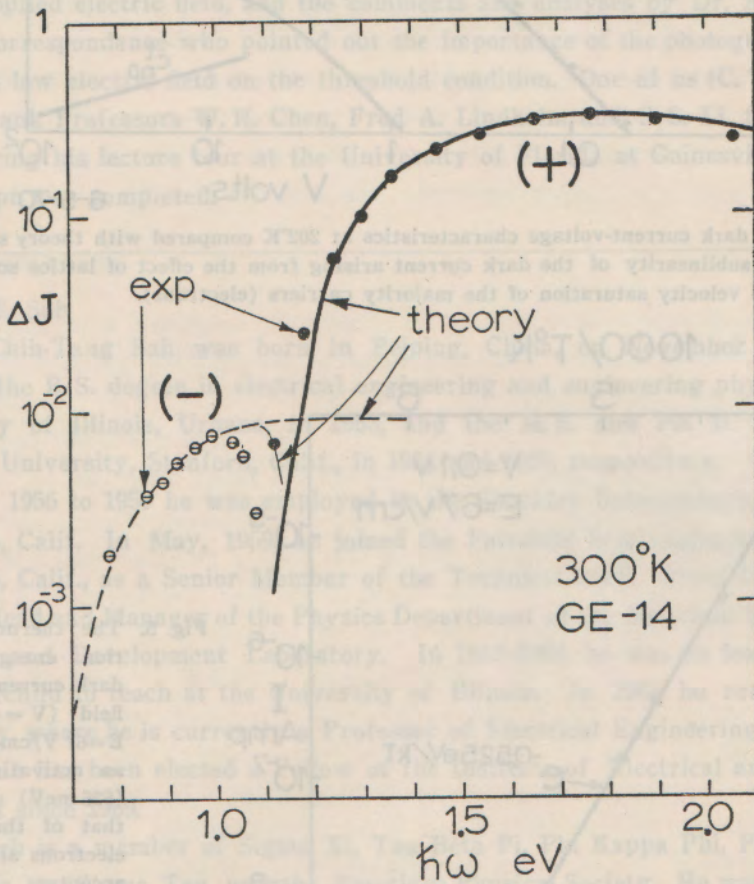


Fig. 3. The data of Barrett and Gerhard of General Electric compared with the theory at 300°K.

The sublinearity of the dark current observed at 202°K on our sample is compared with theory in Fig. 4. The sublinearity comes mainly from electron drift velocity saturation in high electric field as indicated by the middle solid curve in this figure. It is partly dependent on the slight decrease of the electron thermal capture rate at the gold acceptor level, c_{n0}^t , in high electric field.

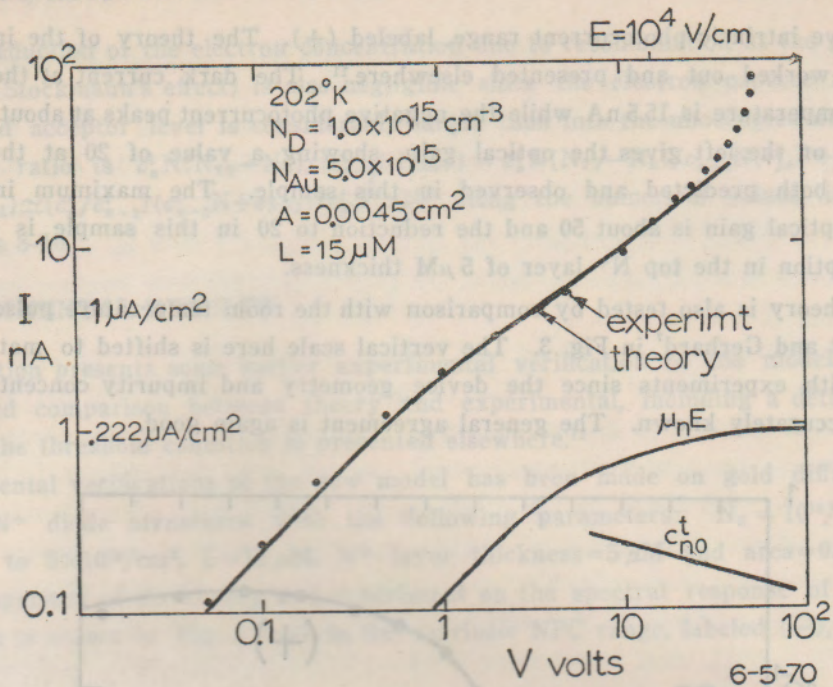


Fig. 4. The dark current-voltage characteristics at 202°K compared with theory showing the sublinearity of the dark current arising from the effect of lattice scattered drift velocity saturation of the majority carriers (electrons).

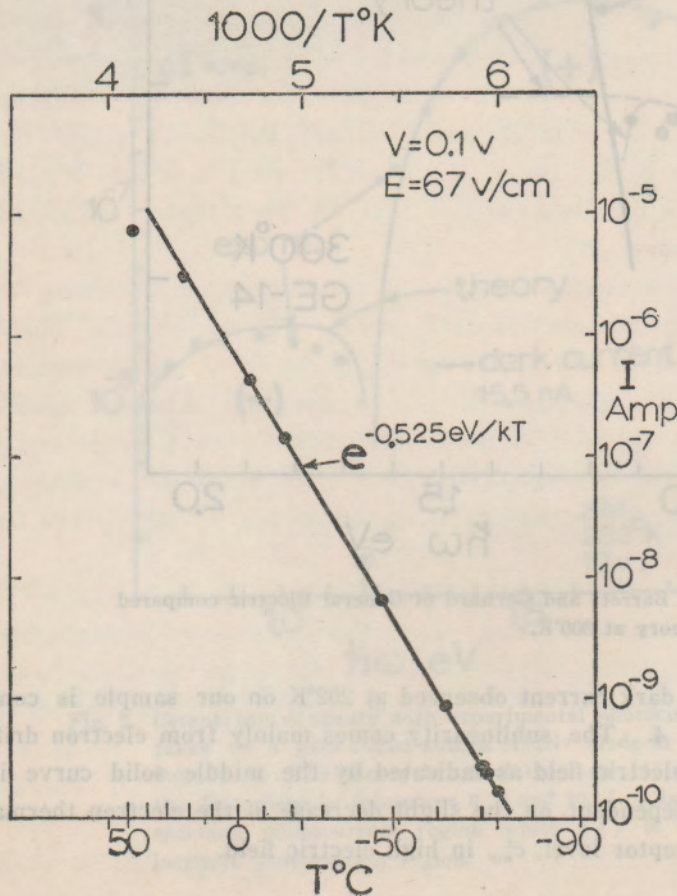


Fig. 5. The thermal activation energy of the dark current at a low field ($V = 0.1$ V and $E = 67$ V/cm) showing an activation energy (525 meV) similar to that of the trapped electrons at the gold acceptor level in silicon.

The thermal activation energy of the dark current is obtained from its temperature dependences at low electric field shown in Fig. 5. The value of 525 mV compares favorably with the thermal activation of electrons, $E_c - E_T = 545$ mV observed in junction dark and photo current and capacitance transients,^{8,10} while its magnitude is also in agreement with those calculated from these emission and capture rates independently obtained,^{8,10} as indicated in Fig. 4.

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