Photogeneration of Carriers in Vitreous Selenium

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The photogeneration process of mobile carriers in vitreous selenium has been studied. The number of carriers generated increases with applied field and temperature. In the high-field region, the quantum efficiency for long-wavelength light excitation (5400 Å to 6000 Å) is $\exp(\beta E^{\frac{1}{2}}/kT-E_0/kT)$, where E is the applied field, β is a constant, E_0 is an activation energy, k is the Boltzmann constant, and T is the absolute temperature. The electric field range in which this equation applies gets smaller for short-wavelength excitation, and β becomes wavelength-dependent. The expression is similar to that obtained for the Frenkel effect, suggesting that the photogeneration is a field-assisted thermally activated process. The activation energy E_0 decreases linearly with increasing photon energy of the exciting radiation and becomes a constant at higher photon energies. The departure of the quantum efficiency from the above expression in the low-field region can be attributed to a competing loss process which prevents complete collection of the generated carriers.

INTRODUCTION

THE optical and the electronic properties of vitreous selenium have been extensively studied. The optical dielectric constants are well documented.[1] Electronic transport measurements[2,3] indicate that mobile carriers of both charge signs are present and that drift mobilities depend exponentially on the inverse of the temperature, suggesting a thermally activated transport process. Hartke and Regensburger[4] investigated optical absorption and photogeneration of carriers in evaporated vitreous selenium films. In their quantum efficiency measurements they assumed a range-limited model in the collection of photogenerated carriers. They interpret their results on the basis of two assumptions: (1) unity carrier-collection efficiency at high applied fields ($\sim 4\times 10^7$ V/m) for all incident-light wavelengths; (2) the photogeneration itself is field-independent. They further assume that the quantum efficiency is one at a relatively short wavelength, i.e., 4000 Å. Under these conditions the photogeneration quantum efficiency is observed to decrease rapidly as the wavelength of the incident light is increased beyond 4500 Å. Thus, an ever-increasing gap between optical absorption and quantum efficiency results as the photon energy decreases. To explain their results, Hartke and Regensburger propose a model based on a photoconductive and a nonphotoconductive component of photon absorption. They postulated that the photoconductive component has unity quantum efficiency in generating hole-electron pairs and the nonphotoconductive component has zero quantum efficiency.

More recently, Tabak[5] studied transient photocurrents in evaporated Se films. He observed that the photocurrent is proportional to the electric field at low fields and to the square root of the field at high fields. He also found that the low-field photocurrent does not scale with thickness. This is contrary to the result one would obtain if the process is bulk-controlled as was proposed by Li and Regensburger,[6] and Hartke and Regensburger.[4] For a bulk-controlled process, the low-field photocurrent should be inversely proportional to the thickness of the film for a given field.

Tabak attributed the low-field carrier loss to recombination in the surface region. To explain the square-root dependence of photocurrent on electric field in the high-field region, he suggested several possibilities, among them a hot carrier effect and a field-dependent generation process.

The present investigation was initiated in an attempt to elucidate the mechanism governing the photogeneration of mobile carriers in vitreous selenium. In this work, the integrated transient photocurrent was measured as a function of the applied field, the incident photon energy, and the temperature. Since the measurement involved counting the number of carriers that drift across the sample, field-dependent mobilities, if any, had no effect on the measurement.

Emphasis was placed on measuring the photogeneration of holes. A limited number of measurements were made on the photogeneration of electrons; these results will be briefly mentioned.

EXPERIMENTAL PROCEDURE AND MEASUREMENTS

The Se films were prepared by a vacuum evaporation process using aluminum plates as the substrates. The deposited films were amorphous and had very high dark resistivity, of the order of 10^{14} Ω cm.

The experimental arrangement employed in making the photoelectric measurements is shown in Fig. 1. A thin layer (approximately 1000 Å thick) of an organic polymer was first deposited on the Se surface followed by vacuum deposition of a thin gold film, thus forming

[1] W. F. Koehler *et al.*, J. Opt. Soc. Am. **49**, 109 (1959).
[2] W. E. Spear, Proc. Phys. Soc. (London) **B70**, 669 (1957).
[3] J. L. Hartke, Phys. Rev. **125**, 1177 (1962).
[4] J. L. Hartke and P. J. Regensburger, Phys. Rev. **139**, A970 (1965).
[5] M. Tabak, Trans. AIME **239**, 330 (1967).
[6] H. T. Li and P. J. Regensburger, J. Appl. Phys. **34**, 1730 (1963).

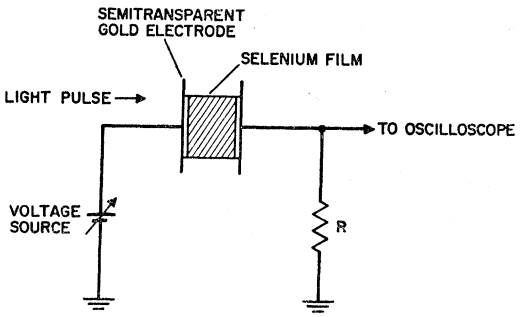

FIG. 1. Schematic of the experimental arrangement.

a semitransparent blocking electrode. A dc electric field was applied to the sample through resistor R.

The photoconductor behaves as a capacitor in the dark and discharges upon light excitation. On exposure to a short-duration light pulse (a few microseconds), the photocurrent induces a voltage across the resistor and the voltage is displayed on an oscilloscope. For every electron or hole (negative or positive polarity, respectively, of the semitransparent electrode) that drifts across the sample, the voltage across the resistor increases by an amount which is equal to the electronic charge divided by the capacitance of the sample. Because of the high-photon absorption coefficient, carrier generation in the Se is confined to a thin region adjacent to the semitransparent electrode. The electric fields applied in these measurements were made sufficiently high (exceeding 10^5 V/m) to insure that all the holes which leave the generation region are collected as indicated by Tabak.[5] The peak voltage measured across the resistor is, therefore, a measure of the number of free carriers generated leaving the absorption region. The charging time constant RC of the circuit is made larger than both the time duration of the pulse and the transit time of the carriers so that the drift of carriers is complete before the circuit starts to recharge the film.

In analyzing the data, the field distribution was assumed to be uniform across the film thickness. This assumption is valid since (1) in all cases the charge transferred is a small fraction of the charge on the electrodes and (2) after each pulse measurement the sample was shorted to allow relaxation of any polarization developed in the sample.

Filtered light sources were used in making the measurements. The half-width of the monochromatized light wavelength distribution was around 100 Å. Mounting the substrate on an aluminum pedestal and partially immersing the pedestal in a cooling bath allowed varying the temperature of the photoconductor. A fast-response thermocouple was attached to the substrate plate for continuous monitoring of the plate temperature. Within the duration of each set of transient pulse height versus applied voltage measurements, the maximum temperature fluctuation was approximately ± 2°C.

RESULTS

Transient Hole Measurements

The number of photogenerated holes drifting across the sample was measured as a function of temperature and applied voltage at eight incident photon energies covering light wavelengths ranging from 5800 to 4000 Å. Samples of the results are shown in Figs. 2–4, where the log of the pulse heights, which is a measure of the number of holes drifting across the sample, is plotted against the square root of the applied voltage. The wavelengths of the incident light in Figs. 2–4 are 5800, 5600, and 5400 Å, respectively. For 5800 and 5600 Å light, the plot indicates a straight-line relationship at each temperature in the high-field region. The extent of the voltage range in which this linear relationship holds is over an order of magnitude. These straight lines can be represented by

$$\Delta V = (eI/C)\exp((\beta E^{1/2}/kT) - (E_0/kT)), \quad (1)$$

where ΔV is the voltage pulse height, e is the electronic charge, I is the number of photons absorbed per cm^2, C is the sample capacitance per cm^2, β is a constant, E_0 is the activation energy, k is the Boltzmann constant, T is the absolute temperature, and E is the applied electric field.

Expression (1) correlates the hole-generation efficiency with the applied field and temperature and is

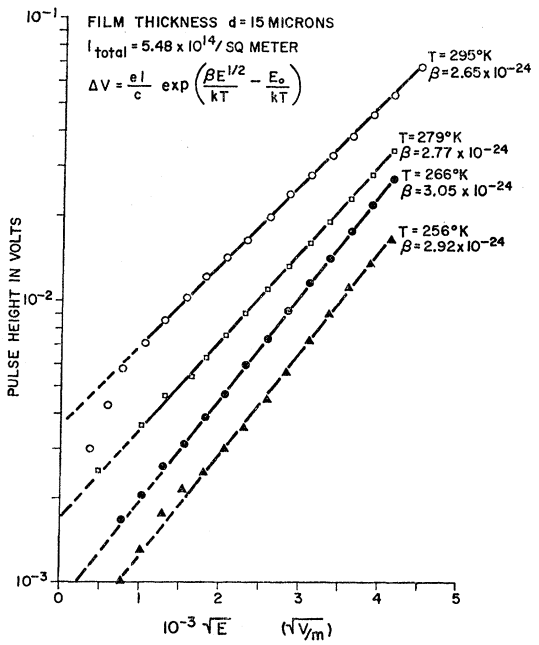

FIG. 2. Voltage pulse height versus square root of the applied electric field. (The pulse height is proportional to the number of carriers drifting across the sample.) Excitation-light wavelength: $\lambda = 5800$ Å.

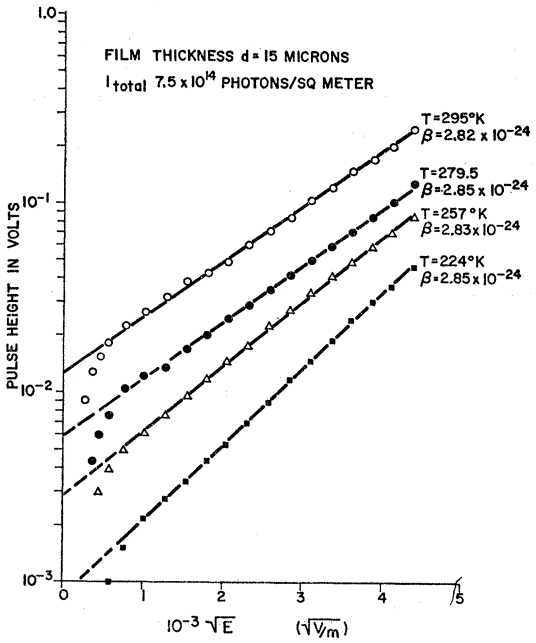

FIG. 3. Voltage pulse height versus square root of the applied electric field. $\lambda = 5600$ Å.

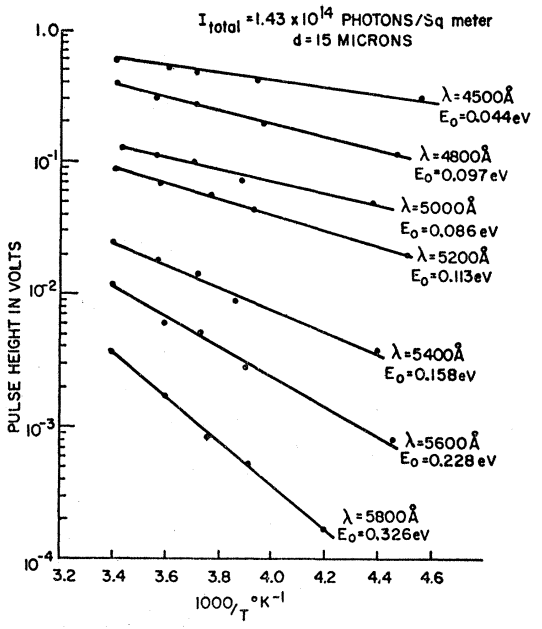

FIG. 5. Voltage pulse height extrapolated to zero electric field versus the reciprocal of the absolute temperature for various excitation light wavelengths.

independent of thickness. For 5400 Å light, the straight-line relationship applies to a narrower range of electric fields. At low fields, the pulse heights depart from those given by expression (1). In this region the pulse height varies linearly with electric field as has been observed by others.[5] This departure could be attributed to some loss mechanism, such as carrier recombination, although the exact nature of it has not been established. Values for β are calculated from the slopes of the straight lines and are shown in the figures. At any one light wavelength, the β's remain essentially constant and are independent of the temperature. This is in accord with the correlation expression presented.

The E_0 values can be obtained by extrapolating the pulse heights in Figs. 2–4 to zero voltages and plotting these values against $1/T$ as shown in Fig. 5. E_0 decreases with decreasing light wavelength or increasing photon energy as shown in Fig. 6.

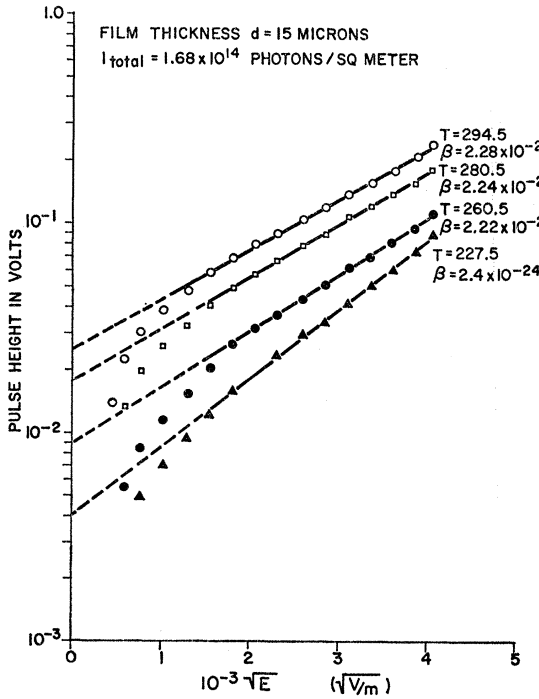

FIG. 4. Voltage pulse height versus square root of the applied electric field. $\lambda = 5400$ Å.

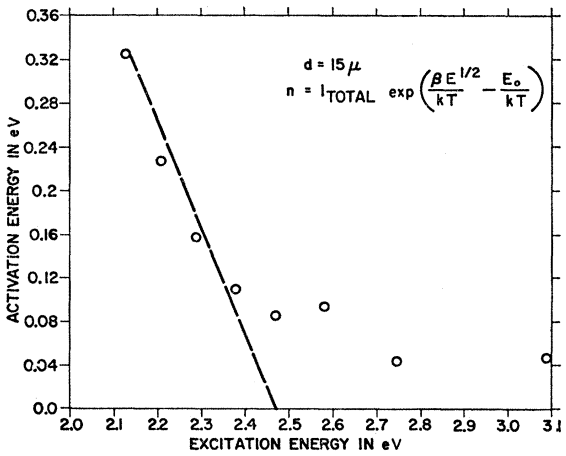

FIG. 6. Activation energy versus incident photon energy.

The logarithms of the pulse heights versus $E^{1/2}$ for shorter wavelength are plotted in Figs. 7 and 8. These are representative of the shorter wavelengths covering 4000–5000 Å. Note that if these data points were plotted as log pulse height versus log electric field, one would observe a linear dependence of pulse height with electric field at low fields. However, at higher fields the dependence of pulse height on the field becomes sublinear with a slope which varies from 0.5 to 0.3, in a limited electric-field range. Thus, by measuring just the short-wavelength photogeneration, one may be tempted to correlate the data using E^{α}, where α is between 0.3 and 0.5. But, for long wavelengths (5200–6000 Å), the high-field dependence is clearly $\exp((\beta E^{1/2}/kT)-(E_0/kT))$ as given by Eq. (1), rather than E^{α}. In view of the long-wavelength results, we thought it more logical to treat the short-wavelength data on the same basis even though the exponential $E^{1/2}$ region gets smaller as the wavelength decreases. A significant temperature dependence of the pulse height was observed even for shorter-wavelength excitation and the activation energies obtained from these plots are also shown in Fig. 6.

Transient Electron Measurements

At room temperature and high fields the effect of the applied field on the pulse height is similar to that of holes, and the generation efficiency is approximately the same in both cases. The main difference occurs in the low-field region where an E^2 dependence is found instead of the E dependence observed for holes.[5] As the temperature is lowered below room temperature, the E^2 region extends to higher fields. At the lowest temperature at which measurements were made (−55°C), the E^2 region extends to the entire range of fields applied.

DISCUSSION

The results for hole generation are summarized below for a clear understanding of the total picture.

(a) At low fields the number of holes drifting across the sample is proportional to the electric field for all wavelengths of excitation.

(b) At high fields the number of holes drifting across the sample is equal to $I\exp((\beta E^{1/2}/kT)-(E_0/kT))$ for all wavelengths.

(c) The onset of the $\exp((\beta E^{1/2}/kT)-(E_0/kT))$ dependence occurs at a lower field for long-wavelength excitation with the result that the range of fields in which the expression holds is larger for longer wavelengths. The range of fields in which this expression holds gets so small at 4000 Å that there is some question as to its validity in this short-wavelength region of excitation.

(d) The β values obtained from the slopes of the log pulse height versus $E^{1/2}$ are 2.85×10^{-24}, 2.84×10^{-24}, 2.29×10^{-24}, 1.75×10^{-24}, and 1.03×10^{-24} (J $m^{1/2}/V^{1/2}$)

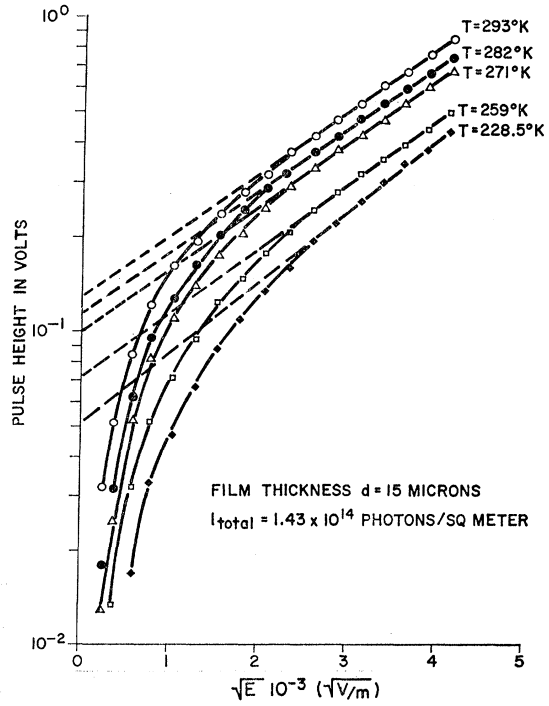

FIG. 7. Voltage pulse height versus square root of the applied electric field. $\lambda = 5000$ Å.

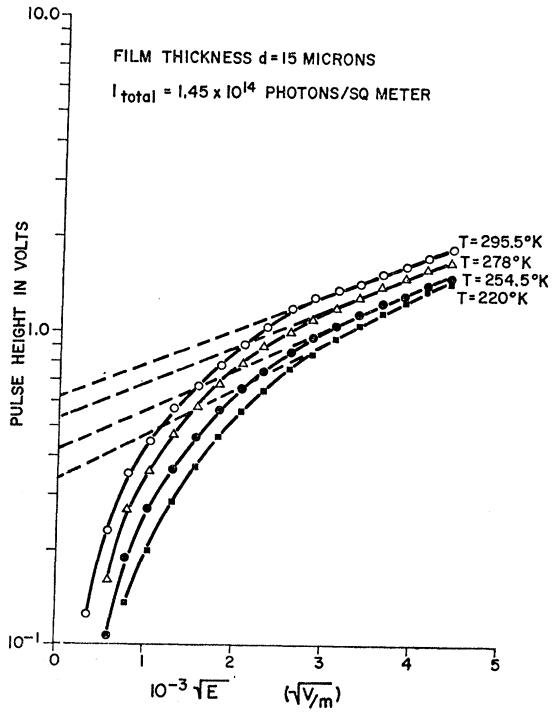

FIG. 8. Voltage pulse height versus square root of the applied electric field. $\lambda = 4500$ Å.

at wavelengths of 5800, 5600, 5400, 5000, and 4500 Å, respectively. Note that the β values are essentially independent of wavelength at long-wavelength excitation and decrease monotonically with decreasing wavelength in the short-wavelength region. For a given wavelength excitation, β is independent of the temperature.

(e) The activation energy E_0 decreases approximately linearly with an increase in photon energy in the region 2.05 to 2.45 eV and then levels off to a constant value at high photon energies. In the linear region, the activation energy is related to the photon energy by $E_0=E_G-E_{ph}$, where $E_G=2.47$ eV.

The results clearly demonstrate the electric-field dependence of photogeneration of mobile carriers in selenium as has also been suggested by others.[7] The departure from this expression at low fields can be attributed to a competing loss mechanism such as recombination in the generation region.

For long-wavelength excitation we have observed a close similarity between the relation obtained and the expression derived by Frenkel.[8] Frenkel considered the electric-field-assisted thermal ionization of charge carriers in electronic semiconductors and insulators. His one-dimensional analysis used the physical model of an electron under the Coulombic influence of a fixed positive charge embedded in a uniform dielectric medium. The solid line in Fig. 9 represents the potential energy of the electron about the positive nucleus in the absence of an external electric field; the dashed line corresponds to the potential in the presence of an applied field, E.

The maximum of the potential energy in the presence of the field is given by

$$e^2/4\pi\epsilon r_0^2=eE \tag{2}$$

or

$$r_0=(e/4\pi\epsilon E)^{1/2}, \tag{3}$$

where ϵ is the dielectric constant of the medium.

The barrier height E_b in the presence of a field is given by

$$\begin{aligned} E_b&=E_0-\Delta E_0\\ &=E_0-(e^2/4\pi\epsilon r_0+eEr_0)\\ &=E_0-\beta E^{1/2}, \end{aligned} \tag{4}$$

where $\beta=(e^3/\pi\epsilon)^{1/2}$. In the absence of applied field, the probability of the electron escaping the barrier because of thermal excitation $=\exp(-E_0/kT)$; the probability of escape in the presence of a field $=\exp((\beta E^{1/2}/kT)-(E_0/kT))$.

A similar mechanism can perhaps be postulated for carrier generation in amorphous selenium. The photon absorption produces a bound electron-hole pair which are freed under the action of the applied field and thermal excitation. In the long-wavelength region, the activation energy plus the photon energy gives the total energy E_G required to create a free hole and a free electron. The E_G value obtained is 2.47 eV and is close to the "band-gap energy" that has been given by Hartke.[4] The appearance of an activation energy for photon energies higher than E_G is not well understood.

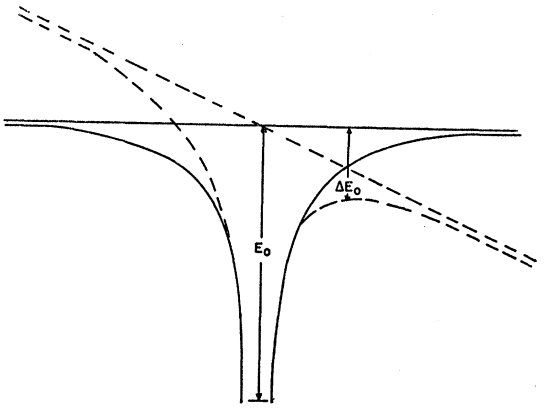

FIG. 9. Frenkel effect showing the energy of an electron bound to a positive point charge in the presence of a uniform applied electric field.

The magnitude of the β values calculated based on Frenkel's expression and using a dielectric constant of 6.3 for Se is 4.85×10^{-24}, whereas experimental β values are 2.85×10^{-24}, 2.84×10^{-24}, and 2.29×10^{-24} (J $m^{1/2}/V^{1/2}$) at wavelengths of 5800, 5600, and 5400 Å, respectively. The measured values of β at long-wavelength excitation are therefore about half the calculated values.

A similar discrepancy in the value of β has been observed in the existing experimental data on the bulk conductivity of Ta_2O_5 and SiO films. Simmons[9] has considered the detailed statistics of population of energy levels in a four-level scheme consisting of valence, conduction band, donor level, and a trap level. In this particular case, he found the probability of thermal excitation in the absence of electric field to be $\exp(-E_0/2kT)$ rather than $\exp(-E_0/kT)$, and in the presence of electric field to be $\exp((-E_0/2kT)+(\beta E^{1/2}/2kT))$. Thus, he accounted for the fact that the experimental β was about half the value given by $(e^3/\pi\epsilon)^{1/2}$. However, for field-assisted thermal excitation of photogeneration in amorphous selenium, this type of analysis will give an activation energy that is twice that obtained using Frenkel's expression.

Hartke[10] has also tried to explain the discrepancy in the value of β obtained for conductivity measurements in Ta_2O_5 and SiO. He considered a three-dimensional model instead of the one-dimensional model used by Frenkel. Hartke's expression for the probability of excitation has essentially two regions, one where the slope is $\frac{1}{2}\beta$ and the second where the slope is β, depend-

[7] M. Tabak and P. Warter (unpublished).
[8] J. Frenkel, Tech. Phys. USSR 5, 685 (1938).
[9] J. G. Simmons, Phys. Rev. 155, 657 (1967).
[10] J. L. Hartke (unpublished).

ing on the field. The range of fields in which the slope is $\frac{1}{2}\beta$ is too small to account for the $\frac{1}{2}\beta$ slope observed in the case of field-assisted thermal excitation in amorphous selenium. Neither of these models can account for the low β values obtained at short wavelengths. Since a realistic model is lacking in the case of amorphous selenium, further attempts to account for the discrepancy are purely speculative.

CONCLUSION

The photogeneration of mobile carriers in amorphous selenium has been shown to be electric-field-dependent. A correlation of the generation of holes and electrons to the applied field, incident photon energy, and the temperature has been obtained. The general feature of the relation suggests a field-assisted thermally activated photogeneration process. The empirical expression obtained experimentally is similar to the one derived by Frenkel for this type of process.

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Photoconductivity Studies of Defects in Silicon: Divacancy-Associated Energy Levels*†

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A new technique using stress-induced reorientation of defect configuration in single crystals and measurement of the photoconductivity spectra with polarized light is developed and is applied to study defects in electron-irradiated silicon. The annealing behavior and the uniaxial stress response of the 1.5-MeV electron irradiation-induced defects causing the $E_c-(0.39$ eV) and the $E_c-(0.54$ eV) energy levels are studied. The results strongly indicate that these two levels arise from different charge states of the same defect having an atomic symmetry around a ⟨111⟩ direction and a transition dipole along a ⟨110⟩ direction. The activation energy for the annealing of the $E_c-(0.39$ eV) level is about 1.25 eV. Correlating these results with those of previous electron-paramagnetic-resonance studies and infrared-absorption studies leads to the conclusion that the defect in question is the divacancy. Further evidence that the 0.32-eV (3.9-μ) photoconductivity band arises from the divacancy in silicon is given. This band is observed in high-resistivity (nominally undoped) p-type silicon, and it anneals in the same temperature region as the divacancy. The results are compared with linear combinations of atomic orbitals (LCAO) calculations. The dominant photoconductivity observed in 45–50-MeV electron-irradiated silicon is found to be an "energy band" that extends from the band edge down to energy of $\approx$0.3 eV, whereas in 1.5-MeV electron-irradiated silicon it is found to be single levels and the energy band is much smaller in both magnitude and extent, extending only down to $\approx$0.8 eV.

I. INTRODUCTION

PHOTOCONDUCTIVITY studies performed during the past several years have concentrated on determining the energy levels of radiation-produced defects.[1–7] No microscopic information concerning the defects has resulted from such measurements. However, Corbett[8] has pointed out that many defects are anisotropic and can be preferentially aligned under a mechanical stress. Photoconductivity spectra measured with polarized light should reflect this alignment and give information about the microscopic configurations

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[1] H. Y. Fan and A. K. Ramdas, J. Appl. Phys. **30**, 1127 (1959).

[2] V. S. Vavilov, A. F. Plotnikov, and V. D. Tkachev, Fiz. Tverd. Tela **4**, 3446 (1962) [English transl.: Soviet Phys.—Solid State **4**, 2522 (1963)].

[3] V. D. Tkachev, A. F. Plotnikov, and V. S. Vavilov, Fiz. Tverd. Tela **5**, 1826 (1963) [English transl.: Soviet Phys.—Solid State **5**, 1322 (1964)].

[4] V. S. Vavilov, Usp. Fiz. Nauk **84**, 431 (1964) [English transl.: Soviet Phys. —Usp. **7**, 797 (1965)].

[5] V. S. Vavilov, S. I. Vintovkin, A. S. Lyutovich, A. F. Plotnikov, and A. A. Sokolova, Fiz. Tverd. Tela **7**, 502 (1965) [English transl.: Soviet Phys.—Solid State **7**, 399 (1965)].

[6] R. F. Konopleva, S. R. Novikov, and E. E. Rubinova, Fiz. Tverd. Tela **8**, 3211 (1966) [English transl.: Soviet Phys.—Solid State **8**, 264 (1966)].

[7] Keiji Matsui, Ph.D. thesis, Université de Paris, 1965 (unpublished).

[8] J. W. Corbett, *Electron Radiation Damage in Semiconductors and Metals* (Academic Press Inc., New York, 1966).