Recombination Luminescence in Irradiated Silicon*†

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Radiative recombination of optically injected carriers has been observed in Co^{60}-γ-ray- and neutron-irradiated silicon. All samples were irradiated at room temperature and stored at room temperature following irradiation. The luminescent spectrum is complex and exhibits sharp structure at liquid-helium temperature. In both n- and p-type float-zone-grown material, the spectrum is dominated by a very intense sharp band located at 0.971 eV. In both n- and p-type pulled crystals the same spectrum appears, but an additional spectrum is found that is shifted to lower energies by 0.180 eV, with a very intense sharp band located at 0.791 eV. The major features of both spectra are independent of the type and amount of doping impurities of valence III or V, and the type and amount of irradiation. The defect associated with the lower-energy spectrum anneals at room temperature, while the defect associated with the higher-energy spectrum is stable at room temperature. An additional band associated with a third defect is found at 0.794 eV in γ-irradiated pulled crystals under certain conditions. Measurements of the luminescence at liquid-nitrogen temperature are consistent with those at liquid-helium temperature. It is suggested that the luminescence of the two major portions of the spectra are due to both phononless and phonon-assisted recombination of free holes and trapped electrons in the ground states of two different defects. Subtraction of the energies of the sharp bands found in the luminescence spectra from the band-gap energy yields 0.194 and 0.374 eV as the energies of the traps below the conduction-band minima.

I. INTRODUCTION

OPTICAL absorption[1–5] and photoconductivity[1,2,6–14] have been extensively used to determine the energy levels and structure of radiation-induced defects in silicon. The complementary phenomena of electron-hole recombination luminescence, found useful in the study of impurity centers,[15–23] has only recently been applied to the problem of radiation damage.

Ivanov and Yukhnevich[24,25] obtained recombination spectra at liquid-nitrogen temperature from Co^{60}-irradiated silicon into which carriers were electrically injected via p-n junctions. The spectra disappeared upon raising the sample temperature to 120°K. They suggested that the luminescence resulted from the recombination of an electron-hole pair bound at a vacancy-oxygen combination, or Si A center.[26,27] It was suggested that phonon-assisted transitions also

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occurred. Further studies produced spectra associated with deeper energy levels of unidentified defects.[28–30]

In the present work, the temperature range of measurements has been extended to liquid-helium temperature, where the recombination process is more efficient and thermal effects are less important. Samples were prepared only from bulk crystals, eliminating the ambiguity associated with the identification of defects in a damaged *p-n* region. The samples were irradiated at room temperature with Co^{60} γ rays or fast neutrons and stored at room temperature until measured at low temperatures. The effect upon the luminescence spectra of type and amount of radiation, interstitial oxygen concentration, and dopant concentration have been measured, yielding information about the structure and production of radiation defects. Preliminary measurements have been previously reported in other papers.[31,32]

II. EXPERIMENTAL PROCEDURE

Electron-hole pairs were excited by an Osram HBO 500-W high-pressure mercury lamp.[33] The light from the lamp, interrupted by a mechanical chopper 135 times/sec, passed through a filter made of two 3-mm thick Jena KG-3 plates[34] separated from each other by 5 cm of water. This filter passed only photons whose wavelengths lay between 3300 and 7000 Å (10% transmission points). The light beam was focused by a pair of glass lenses upon the sample inside a vacuum Dewar. The luminescence emitted from the sample on the side opposite the incident light was collected by a calcium flouride lens and focused with 1:1 magnification upon the entrance slit of a monochromator. A Jarrell-Ash model 82-902, 0.5-m grating monochromator was used for helium-temperature experiments and a Perkin Elmer model 83 monochromator with a fused quartz prism was used for experiments at higher temperatures.

The dispersion of the monochromators was determined from a measurement of the half-width as a function of slit width of the Hg 15 295 Å emission line in a low-pressure mercury lamp. The value was 16 Å/mm for the grating monochromator and about 1000 Å/mm for the prism monochromator.

The light emanating from the monochromator passed through a Jena RG-10 filter[34] 3 mm thick and was then focused by another calcium fluoride lens upon a lead sulfide detector cooled to dry-ice temperature. The RG-10 filter removed any scattered light of wavelength less than 7000 Å. The electrical signal from the lead sulfide detector was amplified by a lock-in amplifier tuned to the reference voltage generated by the mechanical chopper. The output of the lock-in amplifier was displayed on a chart recorder. It is estimated that only 1 photon was detected for about 10^5 photons generated because of reflection losses at the sample surfaces and the geometry of the light-collecting system.

The thickness of the plate-shaped samples ranged between 0.4 and 0.9 mm. The sample thickness had no effect upon the shape of the luminescence spectra because the optical transmission in the 1.2–3.0-μ region of the spectra was governed solely by surface reflection.

In order to reduce the probability of nonradiative recombination of carriers at the surface, the sample was etched in CP4A ($5HNO_3$, 3HF). After the etch was quenched with distilled water, the samples were quickly dried on filter paper and joined to the cold fingers of the vacuum Dewar reservoir with vacuum grease impregnated with finely powdered silver. The intensity of the luminescence of a given sample depended critically upon the etching procedure, but the spectrum of luminescence was independent of it.

The sample temperature with liquid nitrogen in the reservoir was measured with an iron versus constantan thermocouple and with liquid helium in the reservoir with a gold-iron versus chromel-P thermocouple. The temperature was measured for a typical sample 0.5 mm thick under the same experimental conditions as when luminescence data were obtained, but with the thermocouple soldered directly to the center of the sample on the side opposite the incident exciting light. The measured sample temperature at liquid-helium temperature was 6.8°K and at liquid-nitrogen temperature was 78.1°K.

Some samples were irradiated at room temperature by Co^{60} γ rays at the U. S. Naval Research Laboratory and at the Oak Ridge National Laboratory using dose rates of about 10^6 R/h. Others were irradiated by fast neutrons at room temperature in the University of Illinois General Dynamics Triga reactor whose fast-neutron flux was approximately $1.5\times10^{12}/cm^2$ sec while operating at 250 kW. Thermal neutrons were filtered by shielding the samples with 0.030-in.-thick cadmium foil. The samples were re-etched for about 10 sec following each irradiation before obtaining a new luminescence spectrum.

The relative response of the detector-monochromator combination was measured using an Infratron[35] model-404 blackbody source operating at a temperature of 1453°K. These results were used to correct the raw data to allow them to be presented in terms of the relative numbers of photons in a constant wavelength

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TABLE I. Sample histories.

Sample No.	Material class	Boule	Supplier	Resistivity (Ω cm)	Type of irradiation	Irradiation dose	Figure No.
1	*n*FZ[a]	*L*	M[e]	70	γ[h]	10^6–10^8 R	1, 2, 8
2	*n*FZ	*L*	M	70	*n*[i]	10^{12}–10^{14}/cm^2	3
3	*n*FZ	*L*	M	70	*n*	10^{16}/cm^2	3
4	*n*FZ	*B*	D[f]	20	γ	10^8 R	3
5	*p*FZ[b]	*M*	M	70	γ	10^6–10^8 R	
6	*p*FZ	*M*	M	70	*n*	10^{12}–10^{14}/cm^2	
7	*p*FZ	*E*	D	25	γ	10^8 R	
8	*n*P[c]	*T*	M	100	γ	5.4×10^7 R	6
9	*n*P	*T*	M	100	γ	10^6–10^8 R	4
10	*n*P	*T*	M	100	*n*	10^{12}–10^{14}/cm^2	5, 7
11	*n*P	*T*	M	100	γ	10^8 R	6
12	*n*P	*T*	M	100	γ	10^8 R	6, 9
13	*n*P	*T*	M	100	*n*	10^{16}/cm^2	7
14	*n*P	*H*	D	25	γ	10^8 R	7
15	*p*P[d]	*R*	S[g]	250	γ	10^6–10^8 R	
16	*p*P	*R*	S	250	*n*	10^{12}–10^{14}/cm^2	
17	*p*P	*R*	S	250	γ	10^8 R	
18	*p*P	0	M	30	γ	10^8 R	

[a] *n*FZ: *n*-type float zone.
[b] *p*FZ: *p*-type float zone.
[c] *n*P: *n*-type pulled.
[d] *p*P: *p*-type pulled.
[e] M: Monsanto.
[f] D: Dupont.
[g] S: Semi-Elements, Inc.
[h] γ: Co^{60} γ-ray bombardment.
[i] *n*: fast-neutron bombardment.

interval $\Delta\lambda$ as a function of photon energy. Data are presented in this form in all figures.

III. EXPERIMENTAL DATA

A. Organization of Data

The experimental histories of the samples are shown in Table I. They are mainly categorized by type of majority carrier and method of growth. All *n*-type samples were doped with phosphorous and all *p*-type samples were doped with boron.

It is commonly found that silicon crystals pulled from the melt contain oxygen in interstitial positions in concentrations of nearly 10^{18}/cm^3, while crystals grown by the floating-zone technique are known to contain less than 10^{16}/cm^3 interstitial oxygen atoms.[36,37] This fact was previously verified for the samples used here by Hewes[38] from the intensity of the 9-μ oxygen-silicon vibrational absorption band.

Prior to irradiation, the photoluminescence of at least one sample from each boule was observed at liquid-nitrogen temperature. Only the intrinsic band-gap luminescence at 1.10 eV previously reported by Haynes[39] could be observed in the energy range 0.40–1.20 eV.

A number of samples were irradiated for successive times, the luminescence spectra being obtained at liquid-nitrogen temperature after each irradiation and also at liquid-helium temperature following the final irradiation. Other samples were irradiated only once

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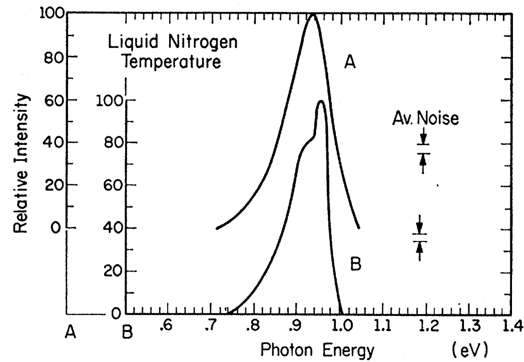
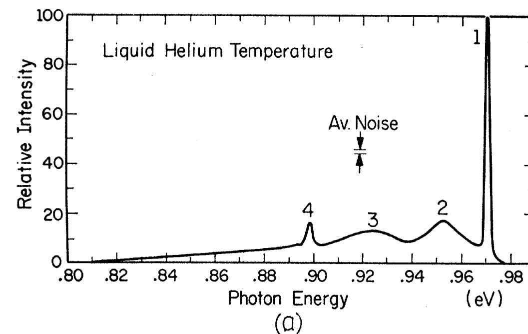


FIG. 1. Luminescence spectra of sample No. 1, 70 Ω cm *n*-type float-zone-grown silicon. Curve A obtained with 920 Å spectral resolution 22 days after Co^{60} γ irradiation of 10^6 R; curve B obtained with 300 Å spectral resolution 20 days after total Co^{60} γ irradiation of 10^8 R.

and analyzed mainly at liquid-helium temperature. Sample Nos. 1, 5, 9, and 15 received successive doses of 1, 2, 7, 30, and 60×10^6 R of Co^{60} γ rays. Sample Nos. 2, 6, 10, and 16 received successive doses of 1, 2, 7, 30, and 60×10^{12}/cm^2 neutrons. The data presented are those which display the most distinguishing features of the luminescence and do not include all the spectra corresponding to each irradiation dosage.

B. *n*-Type Float-Zone-Grown Silicon

The liquid-nitrogen temperature luminescence of sample No. 1, 70 Ω cm *n*-type float-zone-grown silicon,



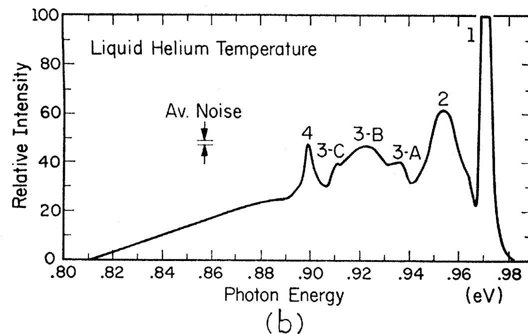


FIG. 2. Luminescence spectra of sample No. 1, 70 Ω cm *n*-type float-zone-grown silicon, obtained with 32 Å spectral resolution after total Co^{60} γ irradiation of 10^8 R; (a) low-signal amplification, 187 days after final irradiation; (b) high-signal amplification, 126 days after final irradiation.

TABLE II. Energy location of luminescence bands of Figs. 2(b) and 3.

Band No.	Band location (eV)	Separation from band No. 1 (eV)	Phonon emitted
1	0.971		zero
2	0.954	0.017	TA[a]
3-A	0.935	0.036	2TA
3-B	0.923	0.048	L[b]
3-C	0.911	0.060	TO[c]
4	0.899	0.072	TO+TA
5	0.884	0.087	TO+2TA

[a] TA: transverse acoustic phonon.
[b] L: longitudinal phonon.
[c] TO: transverse optical phonon.

is shown following γ irradiation in Fig. 1. For the lightest dose of 10^6 R of Co^{60} γ rays, the luminescence spectrum consists of a single asymmetric band peaking at 0.935 eV. The intrinsic band-to-band luminescence has entirely disappeared for this irradiation level. The spectrum for a total dose of 3×10^6 R is similar to that for 10^6 R. Structure is found in the luminescence spectrum following irradiation with 10^8 R of Co^{60} γ rays, the higher luminescent intensity allowing the use of greater spectral resolution. There are at least two bands in the spectrum, one peaking at 0.954 eV and one peaking at about 0.920 eV. The spectra for total doses of 10^7 and 4×10^7 R are similar to that for 10^8 R. The luminescence spectra at liquid-nitrogen temperature of sample No. 2, a 70 Ω cm n-type float-zone-grown sample that was irradiated with fast neutrons, are similar to that of sample No. 1.

The luminescence spectrum of sample No. 1 at liquid-helium temperature is shown in its entirety in Fig. 2(a) and under higher amplification in Fig. 2(b). The energy locations of the bands in Figs. 2(b) and 3 are listed in Table II. The assignment of cooperative phonons to the various bands will be discussed in Sec. IV. The most distinguishing feature of both spectra is the great intensity of band No. 1 centered at 0.971 eV. Band No. 1 is resolution broadened in all spectra presented in Figs. 2, 3, 6, and 7. Consequently, little significance can be attached to the relative intensity of this band compared to the other bands in the spectra.

The luminescence at liquid-helium temperature for sample No. 4, γ-ray–irradiated 20 Ω cm n-type float-zone-grown silicon is given by curve A in Fig. 3. The instrumental spectral width is twice as large as that of Fig. 2(b) and consequently the structure of band No. 3 is barely resolved. The bands labelled 1 through 4, peaking at 0.971, 0.954, 0.923, and 0.899 eV, are the same as those of Fig. 2(b). There is also a weak band, No. 5, which peaks at 0.884 eV. The energy position of this band is also listed in Table II. Band No. 5 is probably not seen in Fig. 2(b) because the luminescence intensity there is smaller due to the higher instrumental resolution. Allowing for the different intensities of the bands because of different resolution, the results are

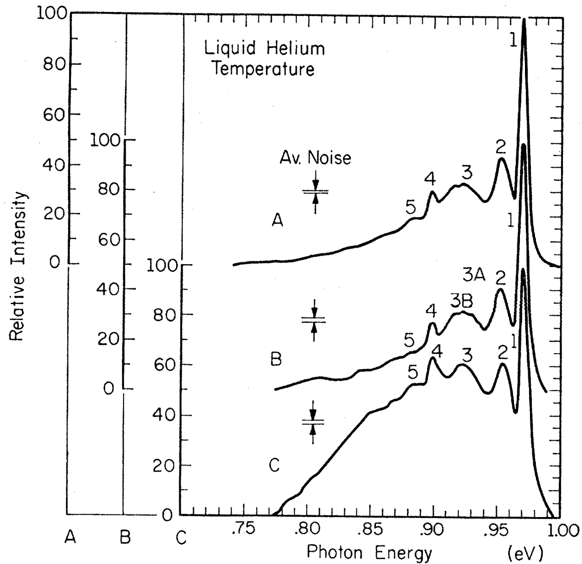


FIG. 3. Luminescence spectra of n-type float-zone-grown silicon, obtained with 64 Å spectral resolution. Curve A, sample No. 4, 20 Ω cm, 36 days after Co^{60} γ irradiation of 10^8 R; curve B, sample No. 2, 70 Ω cm, 257 days after total irradiation by $10^{14}/cm^2$ fast neutrons; curve C, sample No. 3, 70 Ω cm, 181 days after irradiation by $10^{16}/cm^2$ fast neutrons.

the same as for sample No. 1, 70 Ω cm n-type γ-irradiated float-zone-grown silicon.

The luminescence spectrum at liquid-helium temperature for sample No. 2 is given by curve B in Fig. 3. The spectrum after a total dose of $10^{14}/cm^2$ fast neutrons is essentially the same as that of Fig. 2(b) and of curve A in Fig. 3, where the samples have received total γ irradiations of 10^8 R. In particular, the ratios of the peak intensities of band Nos. 1–5 are the same for curves A and B in Fig. 3, which were both obtained with the same spectral resolution. This indicates that the entire spectrum is associated with the same defect and that the same defect occurs in both γ- and neutron-irradiated material for the relatively low fluxes stated above.

The luminescence spectrum of sample No. 3, 70 Ω cm n-type float-zone-grown silicon irradiated with a heavier dose of $10^{16}/cm^2$ fast neutrons is given by curve C in Fig. 3. One reason for the different shape when compared to curve B is that the 0.971-eV band is lower in relative intensity, yet the intensity maximum of all spectra has been normalized to 100 arbitrary units. The background intensity under band Nos. 2, 3, and 4 has grown relative to them and to band No. 1. It is also possible that this background intensity is associated with another defect whose concentration is so small that the defect cannot be detected for fluxes $\leqslant 10^{14}/cm^2$.

No luminescence was observed in any float-zone-grown samples corresponding to photons with energies between 0.80 and 0.40 eV. At dry-ice and ice temperatures, no luminescence was seen in either float-zone-grown or pulled crystals after irradiation.

C. p-Type Float-Zone-Grown Silicon

The liquid-nitrogen temperature spectra of sample Nos. 5 and 6, γ-ray– and fast-neutron–irradiated 70 Ω cm p-type float-zone-grown silicon were similar to those of n-type float-zone-grown silicon, with one exception. In both samples an additional weak luminescence band peaking at 0.83 eV was observed for the lowest irradiation dosages. The liquid-helium temperature luminescence spectra of sample Nos. 5 and 6, as well as sample No. 7, γ-irradiated 25 Ω cm p-type float-zone-grown silicon were the same as sample Nos. 1, 2, and 4 of the n-type float-zone-grown material.

D. n-Type Pulled Silicon

The nitrogen-temperature luminescence spectra of sample No. 9, γ-irradiated 100 Ω cm n-type pulled silicon is shown in Fig. 4. Following an irradiation of 10^6 R, there are new bands at 0.743 and 0.925 eV as well as the intrinsic recombination band at 1.10 eV. It should be noted that the 0.743-eV band was not observed in float-zone-grown samples. After a total dose of 3×10^6 R, the band-gap luminescence has disappeared. The low-energy band does not have a resolved peak. The luminescence spectrum given by curve C is typical of all higher doses of γ rays from 10^7 to 10^8 R. The low-energy band is again distinct and peaks at 0.750 eV. There are also indications of structure on the low-energy side of the main band peaking at 0.946 eV. This band is the same as that observed in the float-zone samples at nitrogen temperature.

The liquid-nitrogen-temperature luminescence spectrum of sample No. 10, neutron-irradiated 100 Ω cm n-type pulled silicon is shown in Fig. 5. In this case there is no distinct low-energy band, but instead a tail extending to 0.60 eV. The major band is the same as that found in all other samples.

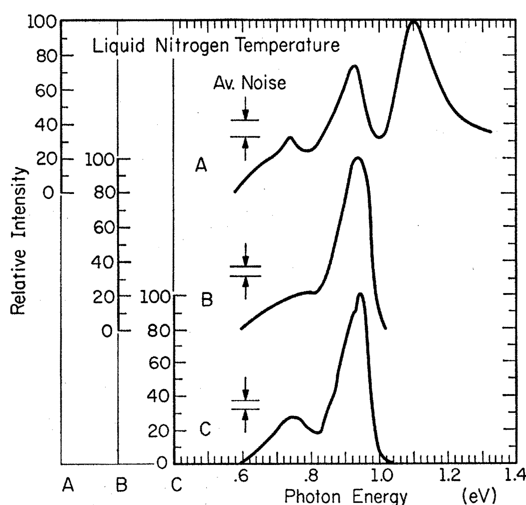


FIG. 4. Luminescence spectra of sample No. 9, Co^{60} γ-irradiated 100 Ω cm n-type pulled silicon. Curve A obtained with 1150 Å spectral resolution 22 days after irradiation of 10^6 R; curve B obtained with 580 Å spectral resolution 28 days after total irradiation of 3×10^6 R; curve C obtained with 520 Å spectral resolution 3 days after total irradiation of 4×10^7 R.

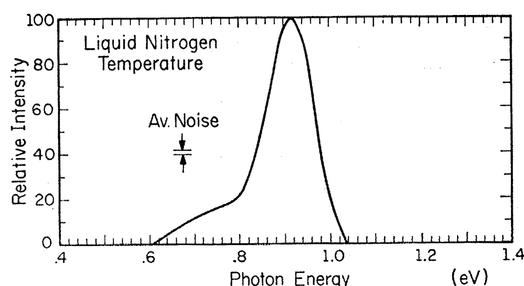


FIG. 5. Luminescence spectrum of sample No. 10, 100 Ω cm n-type pulled silicon. Obtained with 1150 Å spectral resolution 18 days after total irradiation by $10^{14}/cm^2$ fast neutrons.

While studying the luminescence at liquid-helium temperature in γ-irradiated n-type float-zone-grown silicon, it was found that the spectra depended upon the elapsed time after irradiation. This phenomenon is shown in Fig. 6, where the curves are arranged in order according to the elapsed time.

Before discussing the time variation of the curves, the details of a typical curve, B, will be presented. The spectrum was obtained from sample No. 11, γ-irradiated 100 Ω cm n-type pulled silicon, because sample No. 9, from which the intensive nitrogen-temperature data were taken, developed a small hole after repeated etching. The pattern between 0.81 and 1.00 eV is the same as found in the float-zone-grown samples, but the pattern between 0.64 and 0.81 eV was never observed in float-zone-grown samples. Evidently, the defects responsible for the low-energy group of bands are dependent upon the presence of oxygen for formation. The resolution is better at lower energies because the wavelength resolution is constant while the corre-

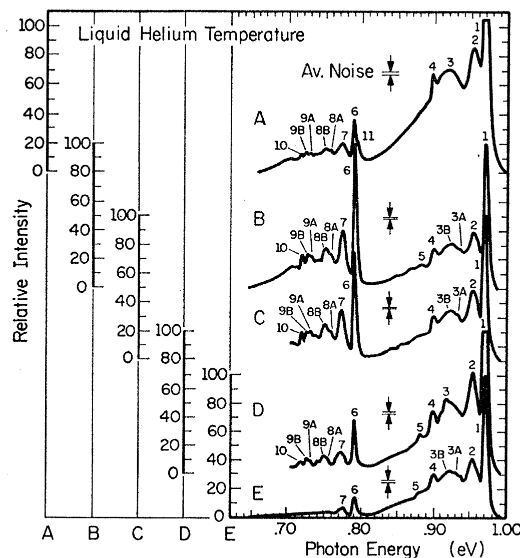


FIG. 6. Luminescence spectra of Co^{60} γ-irradiated 100 Ω cm n-type pulled silicon; obtained with 64 Å spectral resolution. Curve A, sample No. 12, three days after irradiation with 10^8 R; curve B, sample No. 11, 14 days after irradiation with 10^8 R; curve C, sample No. 12, 45 days after irradiation with 10^8 R; curve D, sample No. 11, 80 days after irradiation with 10^8 R; curve E, sample No. 8, 407 days after irradiation with 5.38×10^7 R.

TABLE III. Energy location of luminescence bands of curve B, Fig. 6.

Band No.	Band location (eV)	Separation from band No. 1 in the high-energy pattern (eV)	Separation from band No. 6 in the low-energy pattern (eV)	Corresponding bands	Separation between corresponding bands (eV)	Phonon emitted
1	0.971			6	0.179	zero
2	0.955	0.016		7	0.180	TA[a]
3-A	0.936	0.035		8-A	0.179	2TA
3-B	0.925	0.046				L[b]
4	0.900	0.071		10	0.181	TO+TA[c]
5	0.883	0.088				TO+2TA
6	0.792			1	0.179	zero
7	0.775		0.017	2	0.180	TA
8-A	0.757		0.035	3-A	0.179	2TA
8-B	0.751		0.041			L
9-A	0.730		0.062			TO
9-B	0.727		0.065			0[d]
10	0.719		0.073	4	0.181	TO+TA

[a] TA: transverse acoustic phonon.
[b] L: longitudinal phonon.
[c] TO: transverse optical phonon.
[d] O: zero wave vector optical phonon.

sponding energy interval decreases with decreasing photon energy.

The energies of the peaks of the various bands are listed in Table III. The most striking features are the great intensities of band Nos. 1 and 6, and the high degree of similarity between the two patterns. The energy separation of the various bands from the two most intense bands are also listed in Table III. From these it can be seen that if either pattern is shifted by 0.180 eV toward the other, that many of the features will be replicated. In particular band Nos. 1, 2, 3-A, and 4 will coincide with band Nos. 6, 7, 8-A, and 10, respectively.

The luminescence spectrum of curve B of Fig. 6 was obtained 14 days after irradiation of sample No. 11. The luminescence spectrum of the same sample obtained 80 days after irradiation is given by curve D of Fig. 6. The intensity of the low-energy bands was greatly reduced in comparison to the high-energy pattern. Evidently the defect producing the low-energy pattern anneals at room temperature. The high-energy pattern remained about the same in absolute intensity.

Curve A of Fig. 6 shows the luminescence spectrum obtained 3 days after irradiation under identical conditions for sample No. 12, also cut from the same boule as sample No. 11. It is particularly striking that the intensity of the low-energy group of bands is much lower than the intensity of the high-energy group. There appears to be a new band centered at about 0.794 eV which was not seen in any other samples. The features of the higher-energy pattern are the same as for all other samples. A spectrum not shown here which was taken 5 days after irradiation showed no trace of the 0.794-eV band. It is not possible to state whether this band is present in neutron-irradiated pulled crystals and in float-zone-grown crystals, since no attempt was made to observe luminescence this soon after irradiation in these materials. Curve C of Fig. 6 shows the spectrum obtained on the same sample 45 days after irradiation. It is nearly identical to that of curve B, which was obtained 14 days after irradiation. The low-energy group of bands in curve C is 30% less in intensity than the high-energy group, while in curve B the two groups have nearly equal intensities.

Luminescent data obtained 407 days after irradiation under identical experimental conditions on sample No. 8, cut from the same boule, as sample Nos. 11 and 12, are shown in curve E. The low-energy pattern has further decreased in intensity relative to the high-energy pattern, whose absolute intensity has remained approximately constant.

Evidently, the 0.794-eV band is caused by a third defect which anneals out from 3 to 5 days after irradiation. The defect producing the rest of the low-energy pattern grows until about 2 weeks after irradiation, after which it decays with a time constant on the order of months.

Luminescence spectra in the range 0.40–0.64 eV were not observed in the samples used for determining the data presented in Fig. 6 or in any other pulled-silicon samples.

The liquid-helium-temperature luminescence spectrum of sample No. 14, γ-irradiated 25 Ω cm n-type pulled silicon is shown in Fig. 7, curves A and B. Curve A was obtained 13 days after irradiation and curve B was obtained 90 days after irradiation. These data also clearly demonstrate the room-temperature annealing of the low-energy portion of the luminescence spectrum. There are also some differences in bands 3-A, 8-A, 9-A, and 9-B. Band 3-A did not appear in curve B.

The liquid-helium-temperature luminescence for neutron-irradiated 100 Ω cm n-type pulled silicon is shown in Fig. 7, curves C and D. The luminescence of sample No. 10 after an irradiation of $10^{14}/\text{cm}^2$ neutrons seen in curve C is essentially the same as for γ-irradiated sample Nos. 11, 12, and 14, shown in curves B and C, of Fig. 6 and curve A, of Fig. 7, respectively. There are slight differences in the weakest bands, but this is not considered to be significant due to the rather high noise level. The luminescence of sample No. 13 after an irradiation of $10^{16}/\text{cm}^2$ neutrons in curve D, of Fig. 7 is quite a bit different than sample No. 10. Band 8-A is stronger, while all of the bands in the high-energy pattern are reduced in intensity and tend to be washed

out, just as for the heavily neutron-irradiated n-type float-zone sample shown in curve C of Fig. 3.

E. p-Type Pulled Silicon

The liquid-nitrogen-temperature luminescence spectra of sample Nos. 15 and 16, γ- and neutron-irradiated 250 Ω cm p-type pulled silicon were the same as for sample No. 10, neutron-irradiated 100 Ω cm n-type pulled silicon. There was a low-energy tail extending to 0.57 eV, but no distinct low-energy band at any level of irradiation. The absolute intensity was much weaker than in any other type of material.

At liquid-helium temperature, the luminescence of the p-type pulled sample Nos. 15–18 was too weak to obtain reliable data. As far as could be determined, both the high- and low-energy luminescence bands were present and had the same shape as the n-type pulled samples.

F. High-Resolution Spectra of Intense Bands

A high-resolution spectrum of band No. 1 for sample No. 1, 70 Ω cm γ-irradiated n-type float-zone silicon is shown in Fig. 8(a). The half-width is 0.0045 eV at 78.1°K using an instrumental resolution of 0.0024 eV. The band may be approximated by a Gaussian after subtraction of the background portion of the low-energy tail. If the effective monochromator slit function is also a Gaussian, the true half-width may be obtained by the relation[40]

$$(\Delta E)_t=[(\Delta E)_m^2-(\Delta E)_s^2]^{1/2}, \qquad (1)$$

where $(\Delta E)_t$ is the true band half-width, $(\Delta E)_m$ is the measured band half-width, and $(\Delta E)_s$ is the slit-function half-width. Substituting known quantities into the right-hand side of Eq. (1) yields a value of the true half-width of 0.0039 eV, which is somewhat smaller than kT at this temperature, 0.0067 eV.

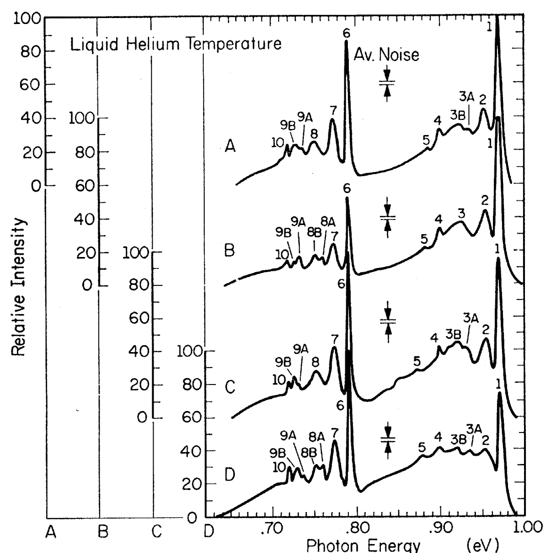


FIG. 7. Luminescence spectra of n-type pulled silicon obtained with 64 Å spectral resolution. Curve A, sample No. 14, 25 Ω cm, 13 days after Co^{60} γ irradiation with 10^8 R; curve B, sample No. 14, 90 days after Co^{60} γ irradiation with 10^8 R; curve C, sample No. 10, 100 Ω cm, 231 days after total irradiation by $10^{14}/cm^2$ fast neutrons; curve D, sample No. 13, 100 Ω cm, 158 days after irradiation by $10^{16}/cm^2$ fast neutrons.

[40] K. S. Seshadri and R. Norman Jones, Spectrochim. Acta 19, 1013 (1963).

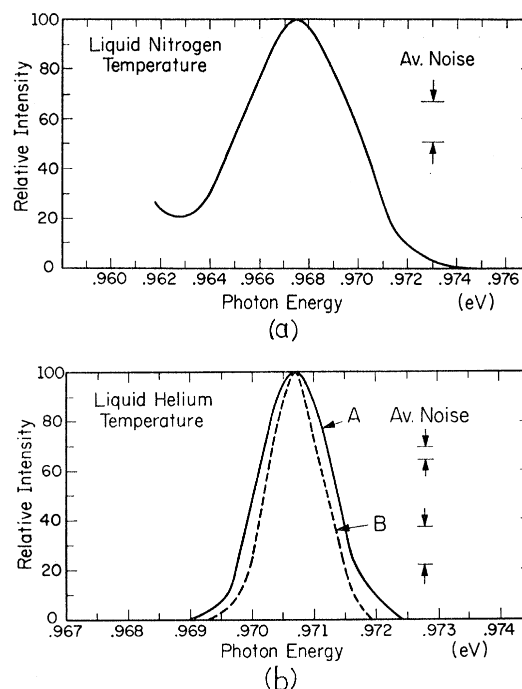


FIG. 8. Luminescence spectra of the intense band No. 1 in sample No. 1, 70 Ω cm n-type float-zone-grown silicon after total Co^{60} γ irradiation with 10^8 R. (a) Sample temperature 78.1°K, 93 days after final irradiation, spectral resolution 0.0024 eV; (b) sample temperature 6.8°K, 305 days after final irradiation, spectral resolution 0.0010 eV for curve A and 0.0005 eV for curve B.

The high-resolution spectrum of this band at 6.8°K is shown in Fig. 8(b). The measured half-width is 0.0014 eV using a resolution of 0.0010 eV and is 0.0011 eV when using as resolution of 0.0005 eV. The true band half-width calculated from Eq. (1) is 0.0010 eV, a value somewhat greater than the value of kT at this temperature, 0.0006 eV.

Both intense bands of sample No. 12, γ-irradiated n-type pulled silicon were studied under high resolution at liquid-helium temperature. The 0.971-eV band is shown in Fig. 9(a). The measured width is 0.0013 eV using a resolution of 0.0010 eV and is 0.0009 eV when using a resolution of 0.0005 eV. These results are the same as for sample No. 1, within experimental error.

The 0.791-eV band of sample No. 12 under high resolution is shown in Fig. 9(b). The measured half-width is 0.0008 eV using a resolution of 0.0006 eV and is 0.0006 eV when using a resolution of 0.0003 eV. The resolution is greater for this band because the energy interval changes as a function of energy when the wavelength interval is held constant. The true half-width calculated from Eq. (1) is 0.0005 eV, or nearly equal to kT.

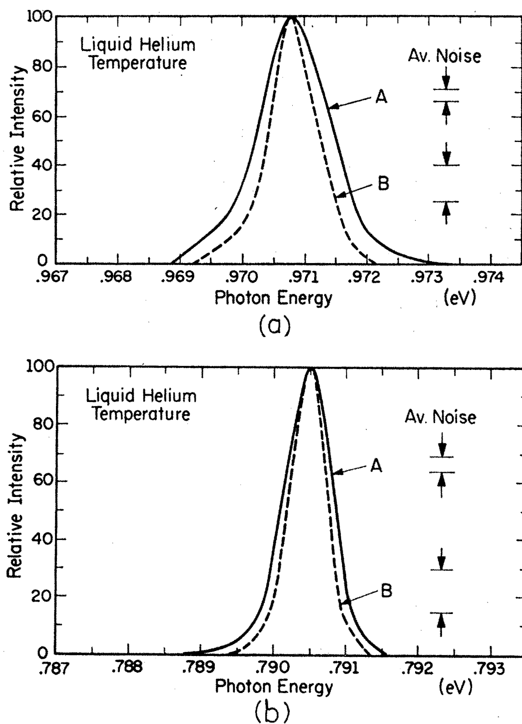


FIG. 9. Luminescence spectra at 6.8°K of the intense bands in sample No. 12, 100 Ω cm *n*-type pulled silicon, 5 days after Co^{60} γ irradiation of 10^8 R. (a) Band No. 1, curve A taken with a spectral resolution of 0.0010 eV, and curve B taken with a spectral resolution of 0.0005 eV; (b) band No. 6, curve A taken with a spectral resolution of 0.0006 eV and curve B taken with a spectral resolution of 0.0003 eV.

It can be concluded, on the basis of the above half-width measurements, that the half-width of the most intense bands is essentially proportional to the temperature at both 78.1 and 6.8°K.

IV. DISCUSSION OF RESULTS

All of the luminescence bands seen after irradiation have an energy much less than the band gap of the material. It can be reasoned, therefore, that the recombination occurs via defects, and that these defects are introduced into the material by the irradiation. As previously noted, there are two major luminescence spectra seen at liquid-helium temperature, one in the range 0.64–0.81 eV and the other in the range 0.81–1.00 eV. Each of the two spectra is associated with a single defect. Before one can use these data to determine an explicit model of the defect or to examine the interaction of the defect with the lattice, it is necessary to determine which of several possible models for recombination is applicable. The correct model must explain the similarity of the two major luminescent patterns, and the intensity and the thermally dependent half-width of band Nos. 1 and 6.

Consider first the possibility that the luminescence results from recombination between a neutral donor-acceptor pair. In order for recombination to occur between neutral donor-acceptor pairs at low temperatures, the concentration of these defects must be such that the ground-state wave functions of the trapped carriers overlap. This critical concentration is about $3\times10^{16}/cm^3$ in silicon when the impurity energy levels are about 0.05 eV from a band edge.[20] The energy positions of the most energetic luminescent bands in the irradiated samples indicates that the sum of the ionization energies of a donor-acceptor pair would have to be at least 0.19 eV. Since the spatial extent of the ground state wave function would be substantially smaller for a defect with an energy level 0.19 eV from a band edge as compared to one only 0.05 eV from a band edge, the concentration of defects would have to be much greater than the estimate given above. The concentration of defects introduced by the irradiation may be estimated in the following manner. Hewes[41] has found the defect-introduction rates to be about 10^6 cm^{-3} R^{-1} for an $E_c-0.17$-eV level in γ-irradiated *n*-type float-zone-grown silicon. The introduction rates for defects with other energy levels and in other types of crystals were smaller than this value. Thus the maximum possible concentration of defects for the highest γ-ray dose of 10^8 R is $10^{14}/cm^3$, well below the required concentration for donor-acceptor pair recombination even if the defect levels were as shallow as 0.05 eV. In the case of neutron bombardment, Wertheim[42] found the defect introduction rate to be a maximum of 5.6 cm^{-1} for levels in the upper half of the forbidden gap. For the largest neutron flux of $10^{16}/cm^2$ used in the present case, the concentrations of defects would be $5.6\times10^{16}/cm^3$. Since luminescence was found for irradiation fluxes about 10^4 times less intense than this maximum, it appears very unlikely that the concentration can be sufficient to give donor-acceptor pair recombination. Furthermore, since both carriers would be localized prior to recombination, the half-width of the luminescence bands should be much smaller than kT at all temperatures. In view of the thermally broadened intense bands found in the present study, and the insufficient concentration of defects produced by irradiation, neutral donor-acceptor pair recombination does not appear to be the mechanism giving the luminescence.

There are three possible ways that electrons and holes may recombine through a single center. These are depicted in Fig. 10. The wave function of a trapped carrier may be represented by an expansion in Bloch functions corresponding to different crystal momenta[43–45]:

$$\Psi_t(\mathbf{r})=\sum_{\mathbf{k}} g_{\mathbf{k}}u(\mathbf{k},\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}, \quad (2)$$

where **k** is the crystal momentum corresponding to a free-carrier energy state in the band nearest the ground-

[41] R. A. Hewes, J. Appl. Phys. (to be published).
[42] G. K. Wertheim, Phys. Rev. 111, 1500 (1958).
[43] V. L. Bonch-Bucevirh, Fiz. Tverd. Tela 4, 298 (1962) [English transl.: Soviet Phys.—Solid State 4, 215 (1962)].
[44] V. L. Bonch-Bruevich and A. A. Drugova, Fiz. Tverd. Tela 7, 3083 (1965) [English Transl.: Soviet Phys.—Solid State 7, 2491 (1966)].
[45] M. Brietnecker, R. Sexl, and W. Thirring, Z. Physik 182, 123 (1964).

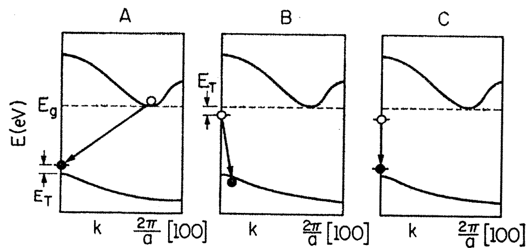


FIG. 10. Schematic representation of possible processes of radiative recombination of carriers via a single recombination center in silicon. A: Free electron-bound hole; B: bound electron-free hole; C: bound electron-bound hole.

state energy level of the trapped carrier and $\mathbf{r}$ is the position vector of the trapped or free carriers. The $u(\mathbf{k},\mathbf{r})$ have the same periodicity as the lattice, and the $g_{\mathbf{k}}$ are weighting coefficients depending on $\mathbf{k}$.

Consider first process A in Fig. 10, the recombination of a free electron with a trapped hole. For a very shallow hole state, the important terms in Eq. (2) will be those near the valence-band maximum and the transition will be one of second order. The momentum selection rule for an indirect transition[46] will be approximately correct and will become

$$\mathbf{k}_e \pm \mathbf{q} = 0, \tag{3}$$

where $\mathbf{k}_e$ is the wave vector of the free electron and $\mathbf{q}$ is the wave vector of the emitted or absorbed phonon. Thus all possible transitions by process A will be accompanied by the absorption or emission of phonons. For a deep level, the wave function of the trapped carrier will contain terms in Eq. (2) corresponding to larger values of $\mathbf{k}$, though the number of terms with a $\mathbf{k}$ value near to that at the minimum of the conduction band will be small. Thus for the case of deep levels there is a posibility for a direct phononless transition. Empirically, Pokrovskii[19,21] has reported that the recombination level must be above the valence-band edge by about $\frac{1}{10}$ the value of the band gap in order to observe these phononless transitions.

The shape of the recombination spectrum may be calculated from classical scattering considerations. The recombination rate per unit volume of electrons in an energy interval dE is given by

$$I(E)dE = N_T n(E) v\sigma(v) dE, \tag{4}$$

where $n(E)$ is the concentration of electrons in the conduction band, E is the electron energy relative to the conduction-band minima, N_T is the number of occupied hole traps, v is the electron velocity, and σ is the cross section for radiative capture of the electron. The photon spectrum $I(\nu)d\nu$, whose functional shape is the same as that of $I(E)dE$, in the case of a band involving no phonons or one phonon, has a half-width of $2.4kT$ if σ is assumed to be constant.[47]

The recombination of a free hole with a trapped electron in an energy level near the conduction band is represented by process B in Fig. 10. The electron wave function will have the form given in Eq. (2), but the sum over $\mathbf{k}$ will now extend to all equivalent minima in reciprocal space. Thus there will be a very large probability for a direct phononless transition. The phononless recombination band, as well as those involving a single phonon, will also have the functional form of Eq. (4) and the same value of half-width. It must be noted that for bands involving phonon emission the following condition must be satisfied during recombination:

$$\mathbf{k}_{\text{phon}} + \mathbf{k}_{\text{def}} = 0. \tag{5}$$

That is, the defect center recoils after emitting the phonon, dissipating its momentum in a local mode vibration or by transferring it to the whole crystal. Pokrovskii[19,21] found experimentally that bound-electron free-hole recombination is more likely to produce a greater relative intensity of a zero phonon band compared to bands associated with phonon processes than is free-electron bound-hole recombination. This is expected theoretically because the bound-electron free-hole recombination is a direct process while the free-electron bound-hole recombination is an indirect one.

The recombination of a hole and electron while both are bound to the same center is depicted by process C in Fig. 10. The energy level of each carrier will be an expansion in Bloch waves as in Eq. (2). There will be a large probability for a direct phononless transition. However, there will be no thermal broadening of the half-width, which consequently will be small in comparison to kT.

The thermally broadened half-width of the intense bands found here eliminates process C as a possible explanation of the data. On the other hand, it is very difficult to distinguish between processes A and B because only qualitative predictions of spectra shape and intensity have been obtained from theoretical studies for the case in which the trapped carrier is deep in the forbidden energy gap.[43,44] However, the fact that the energy levels are deep and the fact that the intense band Nos. 1 and 6 are much greater than the other bands suggest strongly that these intense bands involve no phonons in the recombination process. If, for example, the recombination producing the intense bands involved one of the transverse phonons, then there should also be moderately intense bands involving the other transverse phonon, and no phonons. In particular, the energy separation between two of the bands should correspond to the energy difference of the TO and TA phonons.[48] This is not seen.

It is therefore suggested that each of the two intense bands is caused by the recombination of a free hole and and an electron bound to a defect, the bound electron having an energy level near the conduction band. If

[46] J. Bardeen, F. J. Blatt, and L. H. Hall, in *Photoconductivity Conference* (John Wiley & Sons, Inc., New York, 1956), pp. 146–154.

[47] A. A. Gippius and V. S. Vavilov, in *Radiative Recombination in Semiconductors*, edited by C. B. Guillaume (Dunod Cie., Paris, 1964), pp. 137–142.

[48] B. N. Brockhouse, Phys. Rev. Letters **2**, 256 (1959).

band Nos. 1 and 6 involve no phonons, then the energy levels of the electron would be 0.194 and 0.374 eV from the conduction-band edge, respectively.

After correction for the temperature shift of the silicon band gap, the peak positions of the two most intense bands agree with the observations of Yukhnevich *et al.*[25,29] and Bortnik *et al.*[30] However, the values of the band half-width measured here do not agree with those obtained by these authors, who obtained values of <0.002 eV for the 0.971-eV band and <0.004 eV for the 0.791-eV band. As a result of these observations, they attributed the transition to the recombination of an electron and a hole both bound to an Si A center, after the suggestion of Kurskii.[49,50] In Yukhnevich's model, the hole is in its first excited state, 0.02 eV from the valence-band edge, and the electron is in its ground state, 0.17 eV below the conduction-band minima. This disagreement in the measured temperature dependence between the present work and that reported in Refs. 25, 29, and 30 may arise from the difference in the way in which the data were analyzed. They subtracted a background intensity from the 0.971- and 0.791-eV bands before determining the position of the half-maximum, the background being about one-half of the total intensity under the bands. In the present case, the monochromator slits were narrowed as far as possible while still being able to measure the shape of the intense bands. As seen in Figs. 8 and 9, there is no background intensity at liquid-helium temperature and only about a 10% background at liquid-nitrogen temperature.

The separation of the less intense bands from the intense bands, listed in Tables II and III, when compared to known band edge phonon energies gives support to the proposition that they result from recombination through the same defect levels with the emission of phonons. The probable phonon associated with each band is also listed in Tables II and III. From the well-known phonon density of states for silicon,[48] it is seen that the most intense bands would be expected to be those associated with the TA, TO, and the zero wave vector optical phonon. Though the TA bands are strong, the bands associated with the latter two phonons are weak. Evidently, the probability of phonon emission is controlled by selection rules dependent upon the phonon and defect symmetry.

The Si A center has been found in both float-zone-grown and pulled silicon crystals following bombardment by high-energy electrons[27,51–54] and Co^{60} γ rays.[53–57] This defect may trap an electron in a ground state 0.17 eV below the conduction-band minimum. The energy position of the 0.194-eV level and the fact that this level is also found in n- and p-type pulled and float-zone-grown silicon suggest that it arises from the Si A center. The distance below the conduction band for this level is somewhat greater than that usually found by transport experiments, which measure an ionization energy. Such measurements may give values less than the value seen here because of the cooperation of lattice vibrations in ionizing the center. Infrared absorption and photoconductivity studies have indicated energy levels in the range 0.16–0.22 eV below the conduction-band minima.[58] Thus 0.194 eV is consistent with the values obtained by other optical methods. It is always possible, however, that the defect responsible for the higher energy spectrum is not the Si A center.

The structure of the defect associated with the 0.374-eV level is unknown. The divacancy[5,59–61] and the Si E center,[27,62] a vacancy-phosphorous combination, both have electronic states in this region of the forbidden energy gap. However, they cannot be the defect seen here because they do not need oxygen for formation, and they are stable at room temperature. The divacancy is produced in larger numbers in float-zone crystals than in pulled crystals because of lack of oxygen to form Si A centers, while the Si E center is found only in phosphorous-doped crystals. On the other hand, the 0.374-eV level found here is found only in pulled material and is independent of phosphorous-dopant concentration. There are other unidentified levels reported near this one, but none is known to anneal at room temperature or to need oxygen for formation.[58]

The 0.81–1.00 eV pattern has been observed by Yukhnevich *et al.*[29] and by Bortnik *et al.*[30] at liquid-nitrogen temperature in both bulk material and p-n junctions. They observed the 0.64–0.81 eV pattern only after annealing at 400 and 450°C, respectively. They observed another pattern in the region 0.42–0.53 eV previous to annealing, which was never observed in the present case.

Band No. 11 in Fig. 5, which was seen at liquid-helium temperature up to 3 days after γ irradiation, was not observed by Yukhnevich *et al.*[29] and Bortnik

[49] Yu. A. Kurskii, Fiz. Tverd. Tela 6, 1485 (1964) [English transl.: Soviet Phys.—Solid State 6, 1162 (1964)].
[50] Yu. A. Kurskii, Fiz. Tverd. Tela 6, 2263 (1964) [English transl.: Soviet Phys.—Solid State 6, 1795 (1965)].
[51] G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961).
[52] J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. 121, 1015 (1961).
[53] H. Saito, M. Hirata, and T. Horiuchi, J. Phys. Soc. Japan Suppl. III 18, 246 (1963).
[54] H. Saito and M. Hirata, J. Appl. Phys. (Japan) 2, 678 (1963).
[55] E. Soner and L. C. Templeton, J. Appl. Phys. 34, 3295 (1963).
[56] R. H. Glaenzer and C. J. Wolf, J. Appl. Phys. 36, 2197 (1965).
[57] M. Hirata, M. Hirata, and H. Saito, J. Appl. Phys. 37, 1867 (1966).
[58] See, e.g., V. S. Vavilov, *Effects of Radiation on Semiconductors* (Consultants Bureau Enterprises, Inc., New York, 1965), pp. 186–188.
[59] G. Bemski, B. Szymanski and K. Wright, J. Phys. Chem. Solids 24, 1 (1963).
[60] G. D. Watkins and J. W. Corbett, Phys. Rev. 138, A543 (1965).
[61] J. W. Corbett and G. D. Watkins, Phys. Rev. 138, A555 (1965).
[62] G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. 31, 86 (1961).

et al.[30] An additional band found by then to be centered at 0.795 eV at 77°K would be centered at 0.799 eV at 6.8°K. It is very unlikely that band No. 11 seen in these measurements corresponds to the 0.795-eV band reported by the above workers. The 0.794-eV band is believed to be associated with a recombination level 0.371 eV from a band edge.

It is of interest to compare the present results with those of Hewes,[38] who studied the photodecay lifetime in γ-irradiated samples cut from the same silicon boules used here. He found radiation-induced energy levels 0.17 and 0.4 eV below the conduction-band edge in n-type material. In p-type material, the energy levels were found to be 0.3 eV below the conduction-band edge and 0.18 eV above the valence-band edge, although the latter level could possibly have been located near the conduction band edge. Thus the results reported here for n-type material agree with those reported by Hewes, but the results reported here for p-type material do not agree with his. It may be that this discrepancy results from a strong dependence of the lifetime upon Fermi-level position, while the luminescence spectrum may be essentially independent of the Fermi-level position. The fact that luminescence spectra from the same defect energy level are seen in both n- and p-type material may be explained by considering the way in which recombination occurs through the defect. For small defect concentrations in n-type material, the Fermi level is located above the defect level at low temperatures. There is always an electron trapped at the defect, which may recombine with an externally generated free hole. In p-type material, the Fermi level lies below the defect level under similar experimental conditions. An externally generated electron is first trapped by the defect before recombining with an externally generated free hole. The luminescence spectrum will be the same in both cases.

The absolute intensity of the luminescence was about the same as that of the band-gap luminescence prior to irradiation. Since the band-gap luminescence disappeared after the samples received a sufficient radiation dosage, recombination through radiation defects is more effective than band-to-band recombination in competing for the total radiative probability. Either probability is very small, however, compared to the nonradiative transition probability.

In general, the luminescence spectra appear to depend mainly on the local environment of the radiation defects and upon the phonon spectrum of the crystal. They appear to be less sensitive to the exact nature of the defect. This is reasonable, however, since the charges are not strongly coupled to the lattice.

The variations among samples of band Nos. 3, 8, and 9 are not understood, nor is the origin of the 0.83-eV band in p-type float-zone-grown silicon at liquid-nitrogen temperature.

V. CONCLUSIONS

From this study, it has been found that the defects which act as radiative recombination centers in damaged silicon are generally independent of type and amount of III-V dopant impurities, and the type and amount of radiation, within the range of those parameters used here.

The luminescence spectra in the region 0.81–1.00 eV at liquid-helium temperature belong to one defect and arise from both phononless and phonon assisted transitions. This defect is stable at room temperature and is found in both float-zone-grown and pulled crystals. The energy level of the defect is 0.194 eV from a band edge. Because the phononless component of the spectra is very intense and is thermally broadened, the transition producing the luminescence is most likely the recombination of a free hole and bound electron, and the energy level is most likely near the conduction band.

The luminescence spectra in the region 0.64–0.81 eV at liquid-helium temperature appearing 2 weeks after irradiation belong to a single defect which anneals at room temperature, is dependent upon oxygen for formation, and has an energy level 0.374 eV from a band edge. The phononless component is again very intense and is thermally broadened, indicating that the radiative transition is the recombination of a free hole and bound electron in an energy state near the conduction band.

A luminescence band produced by a third defect appears at liquid-helium temperature at 0.794 eV in γ-irradiated pulled crystals 3 days after irradiation, but disappears 5 days after irradiation. This would suggest a defect at 0.371 eV from a band edge.

The spectra at liquid-nitrogen temperature, though losing some features because of resolution, support the above conclusions. The spectra disappeared at some temperature between 78 and 195°K. No other spectra were found between 0.40 and 1.20 eV.

Note added in proof. C. Jones (private communication) has informed the authors that subsequent high-resolution measurements of the width of the 0.971- and 0.792-eV zero phonon lines reveal that the linewidth increases by only 30% between 6.8 and 30°K but by a factor of nearly 10 between 30 and 80°K. The absolute linewidths, as measured with a higher-resolution instrument, were slightly less than reported above and were always less than kT.

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