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Fine Structure in the Optical-Absorption Edge of Silicon*

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Details of the structure in the indirect optical-absorption edge of silicon were studied by measuring the dependence of the photocurrent in p - n junctions on the energy of the incident photons. The measurements were made at room and higher temperatures for photon energies $0.75 < h\nu < 1.08$ eV. The sensitivity of the method enabled high-resolution measurements in the absorption tail. At room temperature, thresholds were found at ≈ 0.91 , 0.99 , and 1.026 eV. The derivative of the response showed extensive fine structure in this tail. The TO- and LO-phonon-assisted transitions to the ground and excited state of the exciton, previously reported in the phonon emission region, were seen here with phonon absorption occurring around 1.054 and 1.065 eV. There was additional structure of unknown origin in this region.

I. INTRODUCTION

The optical-absorption spectrum near the indirect band gap of silicon was measured by Macfarlane, McLean, Quarrington, and Roberts¹ (MMQR). The absorption arises from indirect allowed transitions with momentum being conserved by the emission or absorption of a phonon. The electron-hole pairs created may either be unbound or exist as excitons with binding energy $\epsilon(n)$, where n denotes the n th exciton level. The theory for the spectral dependence of the absorption coefficient α for such transitions was developed by Elliott.² A summary of the theory and an analysis of the experimental results can be found in the extensive review by McLean.³

The agreement between theory and experiment was, in general, excellent, but there were a few discrepancies. The experimentally determined value of 5.5 meV for $\epsilon(1) - \epsilon(2)$ led to an estimate of ~ 7 meV for the exciton Rydberg, whereas the value calculated from theory by McLean and Loudon⁴ was 14 meV. Another discrepancy involved the absence of any contribution from the longitudinal optical (LO) and longitudinal acoustic (LA) phonons, although transitions aided by these phonons are allowed. Finally, the experimental results showed absorption at photon energies lower than the minimum threshold energy for one-phonon-aided transitions. The value of α in this absorption tail was very small and could not be accurately determined from the transmission technique used by MMQR.

Dean *et al.*⁵ measured absorption and luminescence at low temperatures and obtained results in substantial agreement with MMQR. The higher resolution had enabled them to see additional structure near the thresholds which they attributed to splitting of the ground state of the exciton by valley-orbit interactions. Recently, Shaklee and Nahory⁶ presented results from wavelength-derivative-type experiments which indicated that the

energy separation between the ground and first excited state of the exciton was 11.0 ± 0.2 meV, and the binding energy of the exciton was 14.7 ± 0.4 meV. In addition, they pointed out theoretical reasons that preclude valley-orbit splitting of the exciton ground state. They identified the additional structure near the threshold for absorption of a photon with the emission of a transverse optical (TO) phonon as due to LO-phonon-assisted transitions. These results were later confirmed by Evangelisti *et al.* in low-temperature electroabsorption measurements.⁷

In this work we have investigated the dependence of the photocurrent generated in silicon p - n junctions on the energy of the incident photons. The ratio of the photocurrent to light intensity was measured and corrected to give the response R for constant photon flux. R was taken to be proportional to the absorption coefficient α , which is true as long as the incident light is weakly absorbed. This point is discussed further in Sec. II. The sensitivity of the present method arises from the fact that α is directly related to the measured photocurrent, whereas in transmission or reflection experiments it is related to the small difference between two large measured quantities. The method proved particularly useful for measuring accurately the absorption tail. Measurements were also made in the TO-phonon-absorption region, i. e., where the absorption of a photon is accompanied by the absorption of a TO phonon.

The results can be summarized as follows: (i) At room temperature there are three prominent thresholds in the absorption tail. The first, which is not too well defined, occurs at 0.91 eV, the second at 0.99 eV, and the third at 1.026 eV. The latter two were observed by MMQR. The first lies beyond their range of measurement.

(ii) The dependence of α on the photon energy following the latter two thresholds is not in agreement with that found by MMQR. This is due to the fact that there are a number of other lesser thresh-

olds present.

(iii) In the region from 1.015 to 1.045 eV the results are accurate enough to permit numerical differentiation of the data to get the derivative of the response. The derivative plots show fine structure which has not previously been seen.

(iv) The threshold energies and temperature dependence of α suggest that two- and three-phonon processes give rise to the absorption tail. The fine structure indicates that the phonons participating are not just from the Γ point and Δ symmetry direction of the Brillouin zone, but from throughout the zone.

(v) In the TO-phonon-absorption region our experiments show that there is more structure in the absorption coefficient than accounted for by the theory. Furthermore, it is evident from our data that the fine structure, in the region following TO-phonon-aided transitions to the ground state of the exciton, has been the source of disagreement in previous determinations of $\epsilon(1) - \epsilon(2)$. The value of $\epsilon(1) - \epsilon(2)$ we find is in excellent agreement with that found by Shaklee and Nahory.⁶

(vi) Finally, participation of LO phonons in the absorption process, first recognized by them in the region of phonon emission, is further confirmed in these experiments in the region of phonon absorption.

II. EXPERIMENTAL DETAILS

Commercially available large-area silicon *p-i-n* photodiodes and epitaxial *n-on-p* wafers were used. The *n* epitaxial layer was either phosphorous or arsenic doped, and its thickness was approximately 15 μ . The substrate was always boron doped and its thickness was of the order of 250 μ . The resistivities of the epitaxial layer and the substrate were the same in each sample and ranged in value between 1 and 10 Ω cm for different wafers. The measurements were made with the samples at room temperature and at higher temperatures.

A tungsten lamp, a chopper, and a double-grating monochromator with a spectral bandwidth of 0.5 nm were used to provide a chopped light beam. A beam splitter was used at the exit slit to irradiate the sample and a reference thermopile. The voltage developed across a load resistor connected across the sample was measured with one lock-in amplifier and the output from the thermopile on a second lock-in amplifier. The ratio of the outputs from the two lock-in amplifiers was measured with a ratiometer and recorded. This reading was multiplied by $1/\lambda$ to give R , the response at different wavelengths for constant photon flux. The illumination level was kept low enough that the photocurrent varied linearly with light intensity. R is then proportional to the total number of electron-hole pairs created within an effective collection region

near the junction.

The reasons for taking R to be proportional to α are as follows: In traversing a distance l the light is attenuated from intensity I_0 to $I(l)$, where $I(l) = I_0 e^{-\alpha l}$. In the region of interest α is less than 1 cm^{-1} , and with wafer thickness of 250 μ , we have $\alpha l \ll 1$. Hence $I_0 - I(l) \approx I_0 \alpha l$, and the light absorbed in the effective collection region is proportional to α . We assume the quantum efficiency to be independent of photon energy. This assumption is substantiated by the photoconductive measurements made on germanium by Moss and Hawkins.⁸ They found that in the absorption tail their calculated absorption coefficient from photoconductive measurements was identical to that obtained by Macfarlane *et al.*⁹ from transmission measurements. In the present work the fact that the response is proportional to the number of photons absorbed in the effective collection region and is independent of diode parameters was experimentally verified by shining the light through either surface of the wafer. Despite the large asymmetry of the junction depth relative to the sample surfaces, the response obtained was identical. There were five room-temperature measurements of the response in the region from 1.015 to 1.045 eV. These included the *p-i-n* diode and several different epitaxial wafers. All runs gave results which were the same to within a multiplying factor.

The monochromator which was used in the experiments had a linear wavelength scale. Where extreme accuracy was required the data points were taken by manual setting of this scale. The derivative spectrum was obtained by taking the difference between the responses at wavelengths separated by 1 nm. This gave $\Delta R/\Delta \lambda$ rather than $\Delta R/\Delta h\nu$, but for small ranges of λ one is proportional to the other. The value of 1 nm for $\Delta \lambda$ was chosen for highest resolution consistent with discrimination against noise.

A number of steps were taken to make sure of the genuineness of the structure seen in the derivative plots. The correctness and linearity of the monochromator scale were checked by measuring persistent lines and doublets in atomic spectra. The accuracy and reproducibility of the settings was found to be better than 0.02 nm. Effects due to the grating and beam splitter were eliminated by using a near-infrared transmitting filter and polarizer in front of the entrance slit of the monochromator. This was verified by repeating the experiments with a second thermopile or a Ge photodiode in place of the sample. In neither case was any structure observed. The use of several different samples has already been mentioned. Finally, the samples were heated and measurements made at temperatures 10 to 50°C above room temperature. Large changes in the shape of the ab-

sorption curve are not expected for such small temperature changes and, since the energy gap decreases with temperature, all genuine structures should appear displaced to longer wavelengths. All structures discussed in Sec. III showed this expected behavior. Incidentally, there was no structure found that was caused by the system.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Absorption Tail

The method was useful for photon energies below 1.077 eV. At higher energies α and R are no longer linearly related because of the large value of α , and the large background results in loss of sensitivity. The only information beyond 1.077 eV that was obtained was the energy at which onset of transitions to the ground state of the exciton occurred with the simultaneous emission of a TO phonon. This threshold gave an easily identifiable peak in the $\Delta R/\Delta\lambda$ -vs- λ curve, and occurred at 1.1692 eV. The peak due to the onset of transitions to the ground state of the exciton involving the simultaneous absorption of a TO phonon was easily established and occurred at 1.0538 eV. The average of these two energies gives the room-temperature (296 K) exciton indirect gap, i. e., the energy gap minus the exciton binding energy, as 1.1115 ± 0.0005 eV. Half of the spacing between the two peaks gives the TO-phonon energy to be 57.7 ± 0.5 meV. These values are in excellent agreement with previous results.

A semilogarithmic plot of the response against photon energy in the region of the absorption tail is shown in Fig. 1. There is a measurable response at 0.775 eV, and it increases by about an order of magnitude on going to 0.90 eV. Not much can be said about the shape of the curve in this region, as the signal was too small to be measured accurately. The signal was just above the noise level at the low-energy end and was determined with about 6% accuracy at 0.90 eV.

Towards higher energies the response rises sharply, with clearly observable thresholds at 0.91 and 0.99 eV. Various simple expressions were tried for describing the response between these two thresholds. The formula

$$R = 4.9 + 1.09x + 0.56e^x, \quad (1)$$

with $x = \beta(h\nu - h\nu_0)$, $\beta = 67 \text{ eV}^{-1}$, and $h\nu_0 = 0.925 \text{ eV}$, gave a good fit to the data in the region 0.925–0.983 eV. According to this formula the response is an exponential superimposed on a background consisting of a constant and a linear term. The data in this region at $T = 331 \text{ K}$ were fitted by

$$R = 10.8 + 2.30x + 1.20e^x, \quad (2)$$

where β was again 67 eV^{-1} , and $h\nu_0$ was 0.916 eV. The shift of 9 meV in $h\nu_0$ is in agreement with the

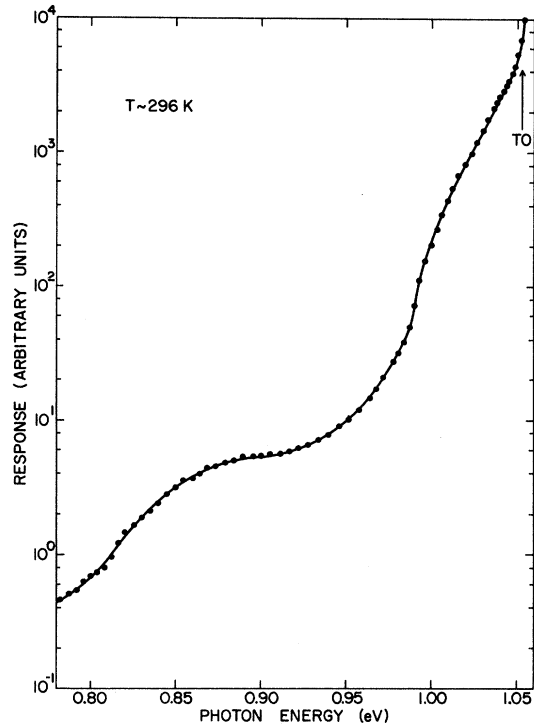


FIG. 1. Photoresponse of silicon p - n junctions in the absorption tail. For reference the arrow points to the TO-phonon-absorption threshold.

change in the energy gap due to the rise in temperature. The latter was measured from the shift of the TO absorption peak and was 9 meV. It is of interest to note that the raising of the temperature increased the response by a factor of about 2.15, as is evident from Eqs. (1) and (2).

The response between the second threshold and the TO absorption region is shown in greater detail in Fig. 2. The top curve is data obtained at 331 K and goes with the upper scale; the bottom curve is the room-temperature data and goes with the lower-energy scale. The top scale is shifted towards lower energy by 9 meV relative to the bottom scale to offset the change in energy gap with temperature; the arrow points to the TO absorption threshold for both the room- and high-temperature data. In the region from 0.99 to 1.05 eV, MMQR fitted their room-temperature data with an expression of the form

$$\alpha = a(h\nu - 0.989)^2 U(h\nu - 0.989) + b(h\nu - 1.021)^2 U(h\nu - 1.021), \quad (3)$$

where $h\nu$ is measured in eV, a and b are constants, and U is the unit step function. This implies that the absorption rises as the square of the energy from thresholds at 0.989 and 1.021 eV. In trying to fit such an expression to our measure-

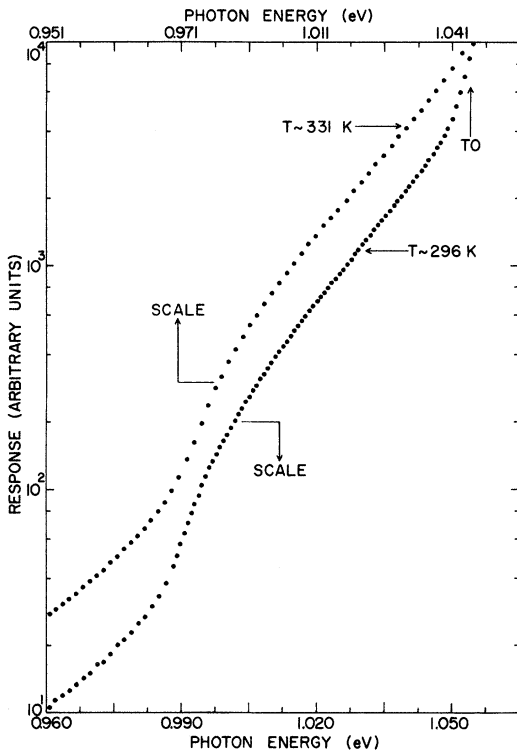


FIG. 2. Expanded plot of response vs photon energy in the region from 0.96 to 1.06 eV. The upper curve has been shifted by 9 meV towards lower energies to offset the decrease in energy gap with temperature.

ments, one of the problems was to find the correct extrapolation of the response at lower energies and subtract it from the actual data. The mechanism giving rise to the absorption below 0.98 eV is not known, and there is some concern about extrapolating an increasing exponential. For want of a better procedure it was assumed that the same mechanism continued to operate beyond 0.98 eV, and the extrapolated value R_{ext} was found from Eq. (1). Figure 3 shows the square root of the difference between the actual and extrapolated values against photon energy. The bottom two curves are room-temperature data for two different samples, the top curve is for a heated sample. The energy scale for the heated sample has again been shifted by 9 meV relative to the scale for the room-temperature data. Between (a) and (b) one can draw approximate straight lines, with nearly common origin for the three curves. The threshold thus established is 0.982 eV at room temperature, as compared to the value of 0.989 eV found by MMQR. There is a break in the curve at point (b). This occurs at 1.0213 eV and coincides with the second threshold of Eq. (3).

To a very rough approximation, one can fit the tail in this region according to the dependence sug-

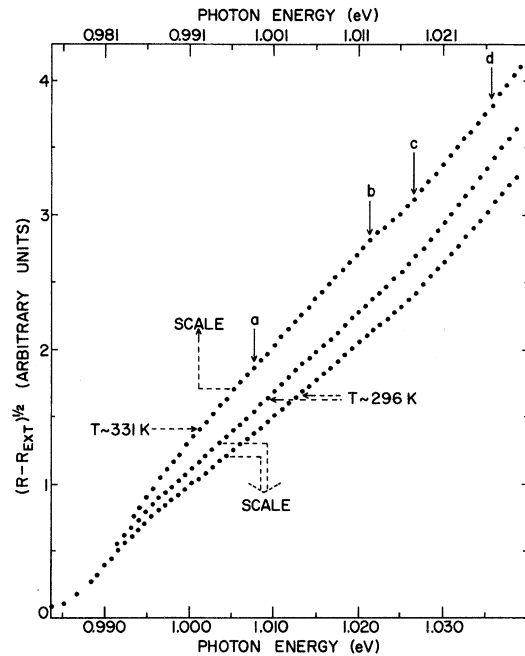


FIG. 3. Square root of the difference between the actual photoresponse and the extrapolated low-energy response from Eq. (1), plotted against photon energy. The bottom curves are for different samples at room temperature. The top curve is for a sample at higher temperature and has been shifted by 9 meV to facilitate comparison with the lower curves. The arrows point to structures seen in all the curves.

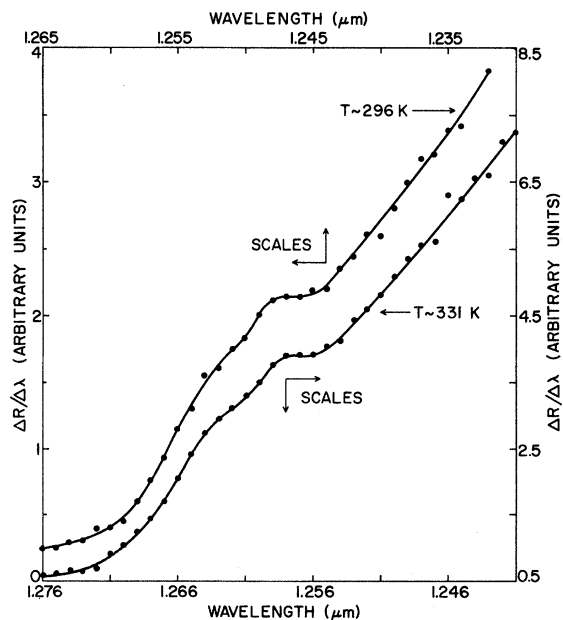


FIG. 4. $\Delta R/\Delta\lambda$ against decreasing wavelength near the threshold at 0.990 eV (1.250 μ). The bottom curve has been shifted by 9 meV towards lower energies. The peaks for the top curve occur at ~ 0.989 and ~ 0.994 eV.

gested by MMQR. The agreement, however, is not very good. There are really no straight-line portions in Fig. 3. There is more structure in the response than indicated by Eq. (3). The arrows point to places where a break is apparent in every one of the curves. The deviations between the experimental values and the curve calculated to give the best fit are well beyond the experimental error.

The structure in the response can be seen more clearly in the derivative plots. As explained in Sec. II, it was more convenient for handling the data to choose λ as the independent variable instead of $h\nu$.

In Fig. 4, $\Delta R/\Delta\lambda$ is plotted against decreasing wavelength in the vicinity of the threshold at 0.99 eV. The top curve is the room-temperature data, and the bottom curve is the data at higher temperature for the same sample. The scales are offset, as in the previous figures, to facilitate comparison. The similarity of these curves is evident. It is clear that not one but two peaks are present. The photon energies corresponding to these peaks are 0.989 and 0.994 eV for the room-temperature data, and are shifted by 9 meV towards lower energies at higher temperature.

Figure 5 shows $\Delta R/\Delta\lambda$ against decreasing wave-

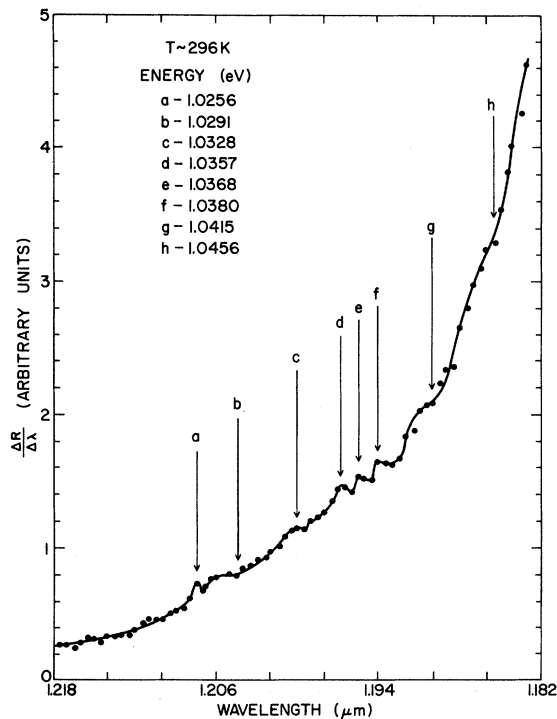


FIG. 5. $\Delta R/\Delta\lambda$ showing fine structure in the absorption tail. The points are experimental values; the line is drawn through features seen consistently in all runs. The photon energies corresponding to the arrows are shown in the figure.

length in the region from 1.22 to 1.18 μ . The points plotted are the average of five runs with each run showing essentially the same features, while averaging eliminated some of the noise. There are several features with different and well-defined shapes; the photon energies corresponding to these features are noted in the figure. It is worth noting that the step increase denoted by (a) occurs at 1.0256 eV, which corresponds to point (c) of Fig. 3. Beyond (h) the derivative is dominated by the TO-phonon peak and its thermal broadening.

The mechanism giving rise to the absorption tail and the fine structure is not known.¹⁰ We can rule out the effects of the electric fields in the space-charge region, as the diodes gave the same results with and without applied bias. Extensive studies of luminescence spectra of pure and doped silicon samples at low temperatures have been made by Dean *et al.*¹¹ The structures seen were identified with levels of excitons bound to neutral impurities, and multiphonon processes.¹² In the present experiments the impurities are ionized, and the energy levels due to bound exciton-ionized impurity complexes in silicon are an open question.¹³ One might expect these to lie near the localized level for a single carrier around the impurity. The observed energies of the structure in the present work do not correlate well with the known levels introduced by the impurities. In addition, the fact that As- and P-doped wafers with resistivities ranging from 1 to 10 Ω cm, and the *p-i-n* photodiode, gave identical results suggests that impurity effects are negligible. Thus although the effect of the impurities cannot be completely disregarded, our results are more in accordance with multiphonon effects as discussed below.

The conduction-band minima in silicon occur in the [100] direction of the Brillouin zone, with the magnitude of the wave vector being about 0.85 times the magnitude at the zone boundary. The optical and acoustic phonons with this wave vector are the ones involved in the one-phonon-aided transitions; the TO phonon has energy 57 meV and the TA phonon has energy 18 meV. It is possible to have two- and higher-order phonon-aided processes, provided the sum of the wave vectors of the phonons is equal to the above value. As pointed out by McLean,³ transitions are possible with the simultaneous absorption of the above TA or TO phonon and an O phonon (i. e., a zero-wave-vector optical phonon). The energy of the O phonon is 63 meV. Two-phonon-aided transition thresholds would be expected at 0.991 eV (for TO+O) and at 1.031 eV (for TA+O); these agree approximately with the data of Fig. 3. The observed threshold at 0.911 eV could be attributed to absorption of three phonons (O+O+TO). The temperature dependence

of the absorption in the region from 0.925 to 0.983 eV is in agreement with this assumption. The probability of the simultaneous absorption of three phonons is given by the product of the occupation numbers n_i of each of the phonons, where

$$n_i = (e^{h\omega_i/kT} - 1)^{-1}$$

and k is Boltzmann's constant. From this the ratio of the absorption at 331 K to that at 296 K is calculated to be about 2.17 as compared to the ratio of 2.15 between Eqs. (1) and (2). Two- and three-phonon structure has been previously reported.^{11,12,14,15} Peaks in modulation, tunneling, and luminescence experiments were identified with combinations of TO, TA, O, and S phonon energies, where S is the phonon connecting different conduction-band minima. The detailed nature of the structure in our results shows that choosing phonons from only some high-symmetry points and directions is inadequate. Calculations of two-phonon effects using a wider sampling of phonons has been done only for Raman scattering, where the sum of the momenta of the phonons is zero. The two-phonon spectra have been observed both in Raman effect¹⁶ and electron energy loss measurements.¹⁷ Calculations along these lines for the absorption edge might be useful in analyzing the present experimental results.

B. TO-Phonon-Absorption Region

It was pointed out in the Introduction that there is some disagreement in the literature with regard to the fine structure in the region of TO-phonon-aided transitions and its interpretation. The data obtained in the present measurements in this region

are shown in Fig. 6 where $\Delta R/\Delta\lambda$ has been plotted against decreasing wavelength. The solid curve in the figure is drawn through those features that are seen with the same shape and relative amplitude in all the results, i. e., different runs on different samples. At higher temperatures these features were present, correctly shifted towards lower energies.

Following the interpretation reported by Shaklee and Nahory,⁶ we identify the peaks at (a) and (b) as the thresholds for transitions to the ground state of the exciton with the absorption of a TO and an LO phonon, respectively. The peaks (d) and (e) correspond to the TO- and LO-phonon-aided transition to the first excited level of the exciton. The energy separation between the ground and first excited level of the exciton is found to be 11.9 ± 0.5 meV. The energy of the LO phonon is calculated to be 55.9 ± 0.5 meV. The values for the phonon energies and exciton levels obtained are in excellent agreement with the values found by Shaklee and Nahory in the phonon emission region.

But there is a discrepancy between theory and experiment. From the theory² it would be expected that the derivative of α would have a $-\frac{1}{2}$ power dependence on the energy from the threshold at (a) to about 12 meV away; and a $\frac{1}{2}$ power dependence on the energy from a threshold 14 meV away from (a). Clearly this is not what happens. Instead at (c), about 6.4 meV away from (a), there is a step increase in the derivative and, neglecting the fine structure, there is an almost linear increase commencing about 10 meV away from (a). This behavior is in good qualitative agreement with the

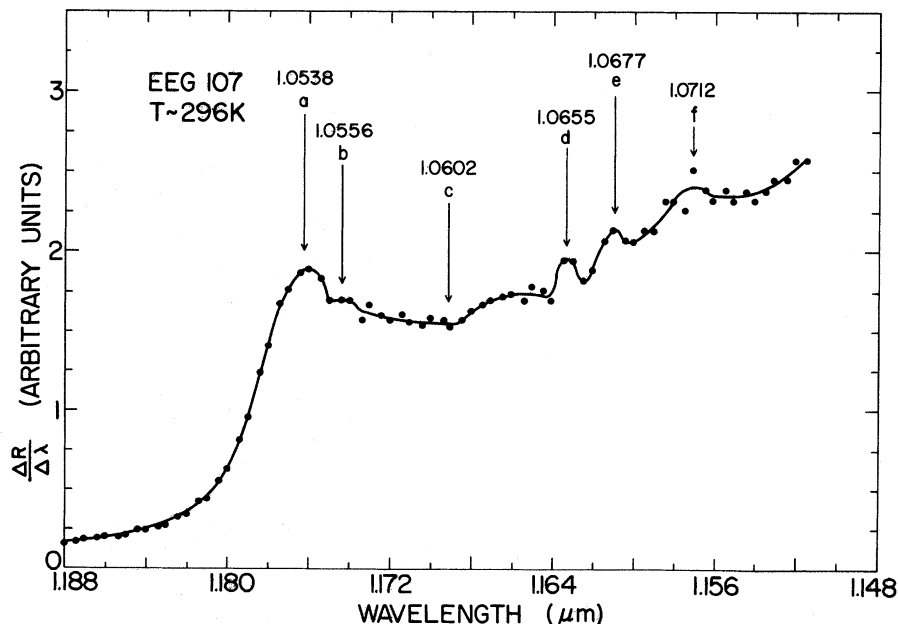


FIG. 6. Derivative of photocurrent with respect to wavelength for a silicon p - n junction, plotted against decreasing λ . The points are measured values of $\Delta R/\Delta\lambda$; the line is drawn through the features seen consistently in all runs. The peaks denoted by long arrows correspond to features seen by previous investigators. The photon energies in eV corresponding to the position of the arrows are shown in the figure.

results of MMQR. They interpreted a steplike increase 5.5 meV away from the TO-phonon peak as the onset of TO-phonon-aided transitions to the first excited state of the exciton, and the almost linear increase in the derivative commencing about 10 meV away from the TO peak as due to band transitions. Dean *et al.*⁵ found a step increase about 7.5 meV from the TO peak with band transitions commencing about 4.5 meV after the step. They also interpreted the step increase as the onset of TO-phonon-aided transitions to the first excited state of the exciton. In Fig. 2 presented by Shaklee and Nahory,⁶ the derivative in the region of TO-phonon emission shows a definite increase, though not steplike, commencing about 7 meV away from the TO peak. It is clear from their figure and Fig. 6 of the present work that the increase is not due to background contributions. Finally, in electroabsorption⁷ spectra of Si a broad negative valley was observed following the TO peak corresponding to transitions to the ground state of the exciton.

Shaklee and Nahory's interpretation of the fine structure is probably the correct one, as it leads to good agreement between the experimental and

theoretical values of the exciton levels, and gives the right energies for the peaks in Fig. 6. There are some features in Fig. 6 which do not correspond to any peaks noted by Shaklee and Nahory. Some of these, like the structure near (f), could be due to multiphonon effects. These effects would be more prominent in the present measurements which were done at elevated temperatures and in the phonon absorption region. However, the increase in the derivative 7 meV away from the TO peak cannot be due to two-phonon effects or impurity effects. If it were, it would appear symmetrically placed with respect to the exciton indirect gap. But, as has been pointed out, it has been observed on the high-energy side of the TO peak in all the experiments, at low and high temperatures, and both in the phonon emission and phonon absorption regions. It thus appears to be related to the TO peak, and consequently to the exciton, but at the moment there is no explanation for it. It is of interest to note that in transmission-type experiments with GaP a crystal whose band structure is very similar to Si, anomalous fine structure was also observed for some of the phonon-assisted transitions.¹⁸

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