Temperature dependence of the band gap of silicon

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The band-gap energy E_g of silicon has been reevaluated with high precision between 2 and 300 K by the following method: the derivative of the absorption coefficient, resulting from free-exciton absorption, has a well-defined singularity, which can be detected unambiguously by wavelength-modulation spectroscopy. The energy of this singularity yields the band gap. Our data deviated by more than 5 meV from the earlier results of MacFarlane et al. and Haynes et al. and fell between their $E_g(T)$ curves. The approximation of $E_g(T) = A + BT + CT^2$ gives $A = 1.170$ eV, $B = 1.059 \times 10^{-5}$ eV/K, and $C = -6.05 \times 10^{-7}$ eV/K^2, for $0 < T \leqslant 190$ K, and $A = 1.1785$ eV, $B = -9.025 \times 10^{-5}$ eV/K, and $C = -3.05 \times 10^{-7}$ eV/K^2, for $150 \leq T \leq 300$ K, which fits our data within 0.2 meV. The major uncertainty of about 1 meV lies in the energies of exciton and TO phonon.

Silicon is one of the first semiconductors on which accurate optical measurements of the band gap were possible. Its band gap was measured by Macfarlane et al.[1] at several temperatures between 4.2 and 415 K. Somewhat later Haynes et al.[2] analyzed the intrinsic recombination of Si to deduce similar band-gap information. The results of these studies differed by more than 15 meV at the higher temperatures. Since then there does not appear to be any published measurements of the band gap of Si over a large temperature range, although much more sensitive optical techniques (i.e., wavelength-modulation spectroscopy) and purer Si samples are now available. It has been the objective of this study to reevaluate the band gap of high-purity Si with a high density of experimental points between 2 and 300 K. This kind of data is necessary not only for technological applications of Si, but also for theoretical efforts at understanding the temperature dependence of energy gaps[3] and other measurements of Si which employ the band gap as a parameter.[4]

The silicon used was high-purity p-type float-zone material with the following specifications: dopant concentrations, $N_A \approx 5 \times 10^{12}$ cm^{-3} and $N_D \approx 1 \times 10^{12}$ cm^{-3}; lifetime of minority carriers, 1500 μsec; dislocation free.

The sample thicknesses were 0.5 and 1.0 cm and the surface areas were 1.0 and 0.5 cm^2, respectively. The surfaces were first lapped with Al$_2$O$_3$ (grit from 5 to 0.25 μ) and then chemically polished.

The measurements were made in the wavelength-derivative mode in transmission. The wavelength modulation was accomplished by vibrating a plane mirror in the Jobin Yvon HRS-1 monochromator about a vertical axis. The amplitude of the wavelength modulation was maintained approximately equal to the spectral slit width. The transmitted signal was detected by a cooled photomultiplier with an InGaAs cathode and was processed through a lock-in in amplifier tuned to the frequency of the wavelength-modulation "wobbler". Because of the limited wavelength range of these measurements and the relatively gradual changes in absolute transmission in this small range, the resulting

data may be viewed to be proportional to the wavelength derivative $d\alpha/d\lambda$ of the absorption coefficient α to a satisfactory degree of accuracy[5] (i.e., the relative magnitudes compared in our analysis are less than one-half a linewidth from one another).

The analysis is based on the theory of Elliott[6] which gives the absorption coefficient α_{FE} describing the portion of the indirect absorption due to indirect free excitons as

$$\alpha_{FE} = a'(h\nu, T) \sum_i (h\nu - E_{gx} - \hbar\omega_i)^{1/2}, \qquad (1)$$

where $h\nu$ is the photon energy, E_{gx} is the free-exciton energy, and $\hbar\omega_i$ are the momentum-conserving phonon energies. The coefficient $a'(h\nu, T)$ is photon energy and temperature dependent, but at any given temperature in our measurement can be considered constant. The first derivative of Eq. (1) gives
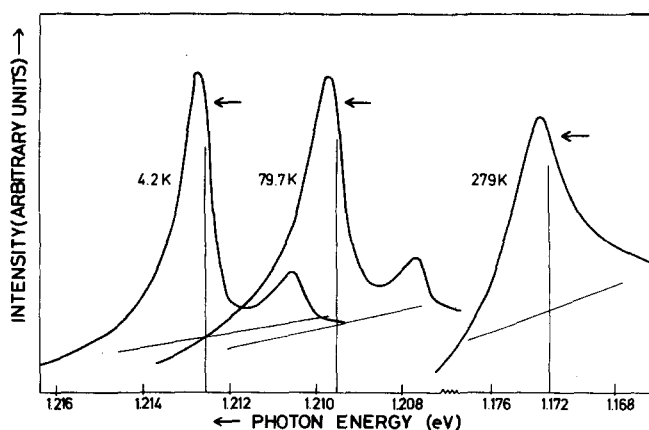

FIG. 1. Wavelength-modulation spectra of the absorption edge of silicon at three temperatures. The large peak corresponds to the TO momentum-conserving phonon emission threshold of free-exciton creation. The peaks may be identified from the work of Shaklee and Nahory (Ref. 5) who studied this spectrum over a larger energy range at low temperature. The graphical construction used to analyze the data is described in the text.
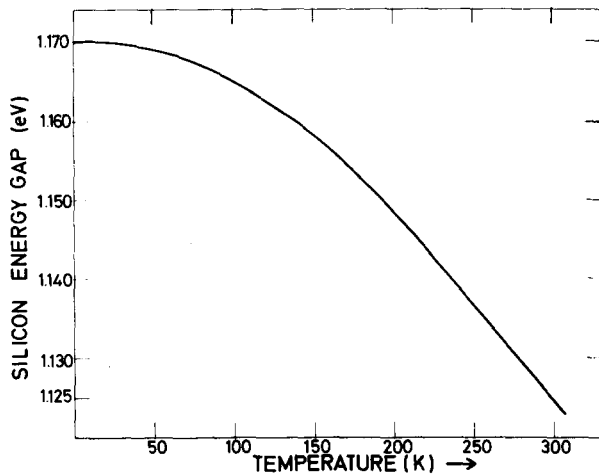
FIG. 2. Temperature dependence of the intrinsic energy gap of silicon.

$$\frac{d\alpha_{FE}}{d\lambda} = a(h\nu, T) \sum_i (h\nu - E_{gx} - \hbar\omega_i)^{-1/2}, \qquad (2)$$

which has a singularity at $h\nu_m = E_{gx} + \hbar\omega_i$. It is this singularity in the derivative which makes the wavelength-modulation technique so sensitive and unambiguous in this case.

The peak of the measured curves has only a finite amplitude because of lifetime broadening of the band-edge density of states. An analysis of such derivative data by Morgan[7] has shown that the actual point of singularity in such a broadened derivative spectrum occurs at 0.88 of the peak on the low-energy side, independent of the magnitude of broadening. Our method therefore provides an unambiguous way of measuring the free-exciton energy, as long as the broadening is sufficiently low so that a well-defined peak occurs in the derivative spectrum.

Examples of spectra obtained with silicon at the energy of the TO momentum-conserving phonon threshold of free-exciton creation are shown in Fig. 1. In each case the procedure of analysis is also shown. First a visual estimate of the background level is made, and then the 0.88 height point with respect to this background is determined to give the value of $h\nu_m = E_{gx} + \hbar\omega_{TO}$. The guess involved in estimating the background is not critical because of the steepness of the edge of the derivative peak. The subsequent analysis then involves determination of E_g, the band-gap energy, from

$$E_g = E_{gx} + E_{xb}$$
$$= h\nu_m + E_{xb} - \hbar\omega_{TO}, \qquad (3)$$

where E_{xb} is the free-exciton binding energy. We have taken $E_{xb} = 14.7 \pm 0.4$ meV and $\hbar\omega_{TO} = 57.3 \pm 0.4$ meV from the work of Shaklee and Nahory,[8] and have assumed the temperature variation of both energies to be negligible between 0 and 300 K.[9]

The measurements were made during slow warmups of the sample in a helium gas environment in a Dewar. The temperature was recorded continuously during the measurement of the spectrum so that the precise temperature and its uncertainty could be determined. The temperature was sensed with carbon and platinum resistors mounted adjacent to the sample. Above 10 K, the temperature change during the time required to record a half-width of the TO phonon peak was typically 0.3 K, but much lower above 100 K. The accuracy of the temperature measurement itself was about 1 K above 100 K and better than 1 K below that temperature.

Figure 1 also shows the peak broadening at higher temperatures; this broadening restricts the measurements to an upper temperature limit of about 300 K.

The resulting analyzed data for E_g in Fig. 2 and Table I are the result of about 140 spectral measurements distributed roughly uniformly between 2 and 300 K, with a somewhat higher density of points below 100 K. The values in Table I are obtained by fitting a least-squares second-order polynomial to 5—7 data points on each side of the temperature in question (i.e., a total of 10—14 points except at the low- and high-temperature ends), and then calculating the band gap at the temperature from the coefficients thus obtained. We used a factor of 12 395.14 eV Å to convert our wavelength data (Å) to energy (eV).[10]

It is often convenient to approximate the temperature dependence with a simple analytic expression. It was, however, impossible to fit the entire curve of Fig. 2 with only one second-order polynomical. We therefore propose the following polynomials which give the energy gap in eV:

$$E_g(T) = 1.1700 + 1.059 \times 10^{-5}T - 6.05 \times 10^{-7}T^2$$
$$\text{for } 0 < T \leqslant 190 \text{ K}, \qquad (4)$$
$$E_g(T) = 1.1785 - 9.025 \times 10^{-5}T - 3.05 \times 10^{-7}T^2$$
$$\text{for } 150 \leqslant T \leqslant 300 \text{ K}. \qquad (5)$$

These polynomials are least-squares fits of our measured data; they approximate the values of Table I up to 0.2 meV within their respective temperature ranges. Note that at higher temperatures the drop of E_g is not linear in temperature; such linearity had previously often been assumed but seems no longer tenable in principle.[3]

TABLE I. Temperature dependence of the intrinsic band gap of silicon, obtained by least-squares fit from rough data (see text).

Temperature (K)	E_g (eV)	Temperature (K)	E_g (eV)
0	1.1701	160	1.1562
10	1.1700	170	1.1544
20	1.1699	180	1.1525
30	1.1697	190	1.1504
40	1.1694	200	1.1483
50	1.1690	210	1.1461
60	1.1685	220	1.1439
70	1.1678	230	1.1415
80	1.1669	240	1.1392
90	1.1659	250	1.1367
100	1.1649	260	1.1342
110	1.1637	270	1.1317
120	1.1625	280	1.1294
130	1.1612	290	1.1269
140	1.1596	300	1.1242
150	1.1579		

Our results are in excellent agreement with single temperature measurements, as those of Shaklee and Nahory,[8] but they differ from the data obtained by Macfarlane et al.[1] and Haynes et al.[2] However, if one considers that Macfarlane et al.[1] used an exciton energy of 10 meV instead of the presently accepted value of 14.7 meV which we employed in Eq. (3), our measurements actually hardly disagree with those of Macfarlane et al. Our data then lie between the data of Macfarlane et al. and Haynes et al.

ACKNOWLEDGMENTS

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[3] See, for example, Y.F. Tsay, B. Gong, S.S. Mitra, and J.F. Vetelino, Phys. Rev. B 6, 2330 (1972).

[4] For example, the problem of deep impurities, their energy determinations, and the search for lattice relaxation require highly accurate values of E_g; S. Braun, H.G. Grimmeiss, and H.J. Queisser (unpublished).

[5] A. Onton and L.M. Foster, J. Appl. Phys. 43, 5084 (1972); see the Appendix for a discussion of the quantitative analysis of wavelength-derivative data of this type.

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[9] P.J. Dean, J.R. Haynes, and W.F. Flood, Phys. Rev. 161, 711 (1967).

[10] The exact conversion formula is $E = hc/n\lambda_0$, where n is the refractive index of air and λ_0 is the vacuum wavelength. n was calculated from Edlén's formula [B. Edlén, J. Opt. Soc. Am. 43, 339 (1953)] and the fundamental constants h and c were taken from Table XX of N. Taylor, W.H. Parker, and D.N. Langenberg, Rev. Mod. Phys. 41, 375 (1969).