from one A site to an adjoining one in the same basal plane as shown by the arrow. We then identify the observed activation energy[8] for the internal-friction peak, 23.5 kcal/mole, with this jump. Again it is consistent with the general picture not to assign this activation energy to the motion parallel to the c axis. The diffusivity in this direction has been estimated[7] to be about 10^{-5} cm^2/sec at 520°C, which is far too high to be consistent with such a large activation energy.

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DIRECT OBSERVATION OF PHONONS IN SILICON BY ELECTRIC-FIELD-MODULATED OPTICAL ABSORPTION*

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In silicon, phonon-assisted transitions from the top of the valence band to the minima of the conduction band have been observed by a number of workers: Macfarlane et al.[1] by optical absorption, Holonyak et al.,[2] Esaki and Miyahara,[3] Chynoweth, Logan, and Thomas,[4] and most recently Logan, Rowell, and Trumbore[5] by phonon-assisted tunneling in p-n junctions; and also Haynes and coworkers by means of recombination radiation.[6,7] The values of the phonon energies obtained agree quite well with those found by Brockhouse by neutron-scattering experiments.[8] In addition to single-phonon processes, multiple-phonon processes have been observed,[4,7] which are also in good agreement with the data of Brockhouse. The most successful experiments have been performed at liquid-nitrogen temperature and below. In this paper we show that some rather accurate determination of the phonon energies can be made at room temperature by means of the electric-field-modulated optical absorption (Franz-Keldysh effect[9,10]). The effect in silicon may be described as photon-plus-phonon–assisted tunneling across the energy gap.

The experimental technique makes use of the electric field in a reverse-biased silicon p-n junction. Since the absorption coefficient of the crystal depends on the magnitude of the field, a monochromatic light beam incident on the plane of the junction can be modulated by application of a small ac voltage superimposed upon the dc reverse bias. The relative modulation of the light intensity is proportional to the change in absorption coefficient $\Delta\alpha$ corresponding to the maximum field E in the junction. This has been discussed in previous papers,[11,12] where this technique was used to investigate the properties of germanium and a detailed description of the experimental arrangement was presented. The silicon samples were n-type wafers of about 50-100 ohm·cm resistivity (~1 cm^2 area, ~70-150 microns thick). A highly doped p layer was diffused on one side to produce a step junction, while on the other side an n^+ region was created to provide a good ohmic contact. The electric field was in the (111) direction, so that all the conduction band minima were equivalent. The reverse dc currents were of the order of 10^{-6} A, and the currents due to the ac modulation at 20 cps were at least an order of magnitude less.

Figure 1(a) shows $\Delta\alpha$ vs photon energy at room temperature. The position of the peaks is practically independent of the magnitude of the electric field. Since both the height and

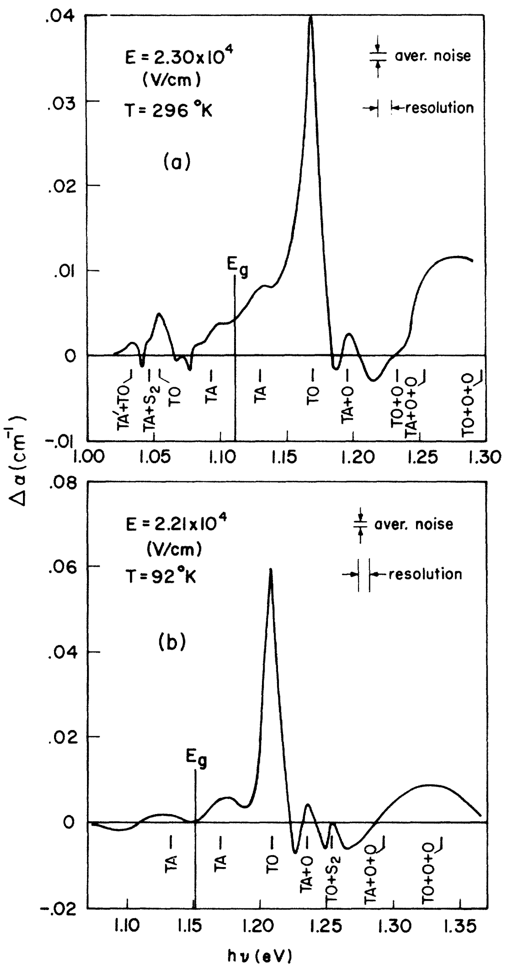

FIG. 1. Spectrum of electric-field-modulated absorption coefficient in silicon p-n junctions at room temperature (a) and at 92°K (b). The energy of various phonon lines observed by tunneling experiments[4] are indicated. TO = transverse optic, TA = transverse acoustic, O = Raman phonon, S_2 = longitudinal acoustic phonon corresponding to scattering between valleys on different axes. E_g = energy gap.

the width of the peaks increase with applied field, the latter was chosen small enough to give good resolution, but not so small as to result in a poor signal-to-noise ratio. The peaks in $\Delta\alpha$ correspond to $E_g \pm E_{ph}$, where E_g = energy gap[13] and E_{ph} = energy of the phonon. The energy of the phonons involved was obtained by taking one-half the distance between the peaks of the absorption and emission processes. Where only one peak was observed, its energy is given as the difference between the peak and the gap energy as obtained by Macfarlane et al.[1] The latter method depends upon the exact nature of the electronic transitions and is therefore only approximate. For comparison, the energies of several phonon processes as observed by tunneling experiments[4] have been indicated in Fig. 1. The majority of these lines are referred to as medium or strong. No evidence has been found in our experiment of some expected weak to very weak peaks. The greatest effect is associated with the transverse optical phonon (TO). Both the phonon-emission and phonon-absorption peaks give a value of the phonon energy very close to the 58.7 meV observed by Brockhouse.[8] The TO interaction is so strong as to partially mask the peaks associated with the second most important phonon process, the TA at 18.0 meV. Haynes also found in recombination radiation[6,7] that the TO phonon gave the largest effect. The broad peak appearing on the high-energy side of the spectrum shown in Fig. 1 has a maximum which is not well defined and lies approximately at 170 meV from E_g. The optical transitions associated with this peak may be multiphonon processes, involving the cooperation of three or more phonons (e.g. TA + O + O and TO + O + O, where O is the Raman phonon). In a recent room-temperature experiment on silicon, Chester and Wendland,[14] using a technique somewhat similar to ours, have been able to observe only the TO peak at ~1.17 eV and just possibly the peak at ~1.195 eV. In particular, they did not observe the processes occurring with phonon absorption (i.e., in the range $h\nu < E_g$). In Fig. 1(b) the spectrum obtained at 92°K is shown. All the lines associated with processes requiring the presence of phonons in the lattice have been reduced or have vanished. The observed phonon energies are summarized and compared in Table I with those given by other methods (some weak or very weak phonon processes not detected in this work have been omitted).

Figure 2 shows the dependence of $[\Delta\alpha]^{1/2}$ on the applied field at the peak energy of the TO processes. The field dependence of the absorption coefficient for indirect band-to-band transitions has been calculated by Penchina,[15] and should follow at the threshold energy an $E^{4/3}$ law. However, Fig. 2 shows that the peak heights are proportional to E_2 and intercept the origin at zero field. The results suggest a first-order Stark effect, which may be associated with exciton states. Since the energy difference between the exciton states and the band edge lies within the resolution

Table I. Comparison between the phonon energies determined in the present research and those previously obtained by other methods (energies are in meV).

Source	TA	TO	TA + S_2	TA′ + TO	TA + O	TO + S_2
Neutron scattering[a] (room temperature)	18.0 ± 0.6	58.7 ± 1.2	···	···	81.3 ± 1.8	···
Tunneling[b] (4°K)	18.4	57.6	65.4	78.6	83.1	102
Tunneling[c] (0.8°K)	18.7 ± 0.2	59.1 ± 0.2	···	···	···	···
Optical absorption[d]	18.2	57.7	···	···	···	···
Present work:						
(a) room temperature	~17.5	58.1 ± 0.6	~66.0	~78.4	~84.0	···
(b) 92°K	···	~57.5	···	···	~84.1	~102.3

[a]See reference 8. [b]See reference 4. [c]See reference 5. [d]See reference 1.

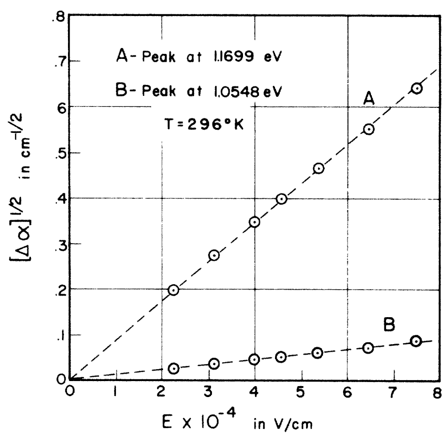

FIG. 2. Square root of the field-induced change in α vs electric field. The data refer to the optical thresholds associated respectively with the emission and the absorption of the TO phonon.

of the apparatus, a distinction between the two processes cannot be made. In conclusion, the method provides a new way of observing the phonons in semiconductors. The measured phonon energies in silicon agree quite well with those obtained by other methods.

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