

the Li⁺ and the Si atoms.^{17,18} The model employed here is very much simplified; however, it does appear to explain, in a qualitative fashion, many of the observed features.

SUMMARY

New absorption bands are observed in boron-lithium-doped silicon. Some of these bands are due to double-quantum transitions in local modes at individual

impurity sites. The relative strengths of the absorption show the greatest anharmonicity in the vibration of the lowest frequency local mode produced by the boron-lithium impurities. Four of the five remaining bands may be ascribed to combinations of the two strongest local modes with silicon critical-point phonon frequencies.

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Defect Structure of Crystalline Quartz. II. Variation of Displacement Threshold Energy with Crystal Growth Rate*

GEORGE W. ARNOLD

Sandia Laboratory, Albuquerque, New Mexico

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An optical-absorption maximum (*C* band) is produced at about 220 $m\mu$ in crystalline quartz by electron bombardment at 77°K. The band is produced by the displacement of lattice atoms and not by ionization. Previously it was shown that the production rate of the band for constant integrated electron flux increases greatly with increased growth rate. In the present experiment, the threshold energy for the displacement which leads to *C*-band absorption was measured in synthetic crystalline quartz grown at 0.45 and 1.91 mm/day. Interpretations of the data lead to the conclusion that *C*-band absorption is caused by displacement of oxygen atoms and that the threshold energy for this displacement is a function of growth rate varying from 15 ± 5 eV for fast-growth (1.91 mm/day) material to 50 ± 5 eV for quartz grown at a slower rate (0.45 mm/day).

I. INTRODUCTION

CRYSTALLINE quartz develops an absorption band (*C* band) in the near ultraviolet when bombarded with fast electrons or neutrons. For electron bombardment, this band lies near 220 $m\mu$. Its characteristics have been discussed in an earlier paper.¹ It was shown there that, for constant time-integrated electron flux, the production rate of the defects responsible for the *C*-band absorption in synthetic quartz increased by a factor of 17 as the growth rate increased by a factor of 4.5. Since the *C*-band absorption was shown to be due to a displacement process, this defect-production-rate variation with crystal growth rate suggests that the threshold displacement energy may also vary with rate of growth. The present paper reports measurements of the threshold displacement energy in synthetic crystalline quartz and its variation with crystal growth rate using the optical absorption of the *C* band produced by electron irradiation.

II. BACKGROUND

The threshold energy E_d , for displacement of a lattice atom is that energy which, when transmitted to the atom, will just dislodge it from its site. The assumptions made in the Seitz-Koehler² formalism in defining the cross section for displacement by relativistic electrons are used. In this paper a step function is assumed for the threshold energy, i.e., no atoms will be dislodged for an electron energy below E_t , which transmits a maximum energy of E_d , and all atoms given an energy of E_d or greater will be displaced with unit probability.

The number of displaced atoms per cm^3 produced by electron bombardment for energies greater than that required for displacement is given by $N_d = N_0 \sigma_d \Phi \bar{\nu}$, where N_0 is the number of target atoms/ cm^3 , σ_d is the cross section for primary atom displacement in cm^2 , Φ is the electron flux in e/cm^2 , and $\bar{\nu}$ is the number of secondary target-atom displacements per primary displacement. The displacement cross section σ_d is a

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¹ G. W. Arnold, *Phys. Rev.* **139**, A1234 (1965).

² F. Seitz and J. S. Koehler, *Solid State Physics* (Academic Press Inc., New York, 1956), Vol. 2, p. 305.

function of the bombarding electron energy and the threshold energy E_d .

Threshold energies for displacement of lattice atoms have been determined for a large number of metals and semiconductors by use of monoenergetic-electron irradiation. There have been, however, very few similar measurements for insulators; Al_2O_3 ³ and diamond⁴ are the only insulators for which values have been reported. The difficulty lies in finding a measurable property which is a function of displacement. In diamond the semiconducting properties of type-IIb stones permit the measurement of electrical conductivity as a function of electron-bombardment energy. These, in conjunction with absorption measurements of an optical band, gave a value of about 80 eV for displacement of carbon atoms in diamond. In Al_2O_3 , optical-absorption measurements gave a value of about 40 eV for displacement of aluminum.

In the case of crystalline quartz, a measurement of the C-band absorption yields the number of displacements N_d , since the latter is directly proportional to the optical-absorption coefficient α for the absorption-band maximum produced by the generated displacements. Thus, a means exists for determining the threshold energy. This is most simply done by carrying out irradiations, for a constant time-integrated electron flux, at various bombarding energies. The ratio of the absorption coefficients at two different energies is equal to the ratio of the number of displacements generated at these energies. One can then compare this ratio with the ratios of theoretically determined values of N_d . These latter ratios are just the ratios of the displacement cross sections since $\bar{\nu}$ is approximately one. Since the cross section is a function of E_d , a fit of experimental data can be made with one of a family of cross-section curves, the best fit yielding the value of E_d .

III. EXPERIMENTAL PROCEDURE AND RESULTS

The synthetic quartz used has been described previously.¹ Samples used for the determination of threshold energy were taken from the two extreme growth rates available, i.e., from the 0.45 mm/day and 1.91 mm/day crystals. These figures refer to average total growth rate in the Z growth direction. The sample thickness was 0.0635 cm, and the orientation was such that the polished faces were perpendicular to the c axis. In choosing an appropriate sample thickness, two considerations are of importance: (1) the sample must be thick enough to give a measurable absorption for reasonable values of electron flux, and (2) it is desirable to keep the sample as thin as possible in order to avoid excessive electron energy loss due to multiple scattering. The latter factor is especially important at low electron

TABLE I. Calculated percent increase in electron path length in crystalline quartz due to multiple scattering.

Incident energy (MeV)	Percent increase in electron path length (0.635 mm thickness)
1.855	13.0
1.348	23.3
0.826	50.7
0.545	99.3

energies as shown in Table I which gives the effects of multiple scattering in which the electron travels greater distances than the measured thickness of the sample, resulting in higher absorption coefficients. The apparent increase in thickness, at various electron energies, has been calculated using the Yang⁵ theory. In the results to be presented, appropriate corrections have been made to take this effect into account. An electron flux of 6.68×10^{17} e/cm² was used in all irradiations. This value was chosen, from a consideration of the C-band growth curves at various growth rates and electron energies,

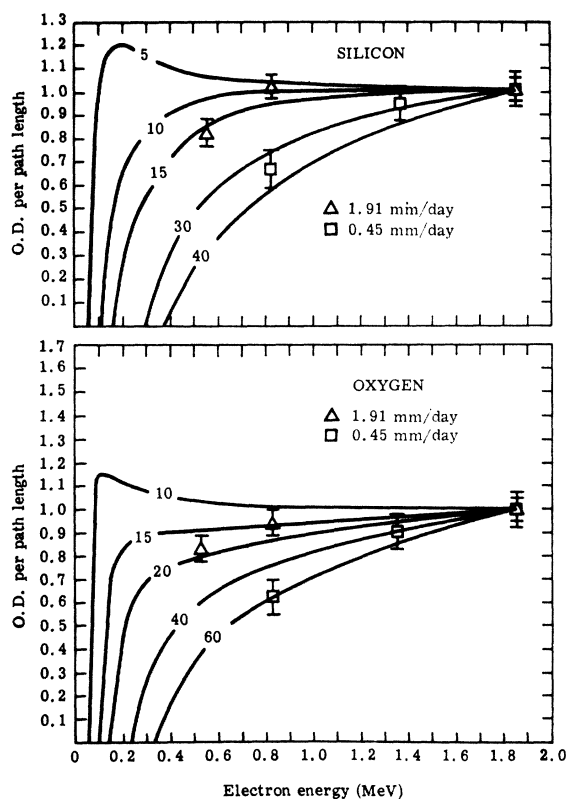


FIG. 1. Optical density (O.D.) per unit path length versus effective electron energy, compared with calculated total cross sections for silicon and oxygen, all normalized to unity at 1.85 MeV. Δ , \square , optical density per unit path length induced by a constant flux of 6.68×10^{17} e/cm², for various effective electron energies, for crystal growth rates of 1.91 and 0.45 mm/day, respectively. Total cross section for silicon and oxygen for various values of E_d .

³ G. W. Arnold and W. D. Compton, Phys. Rev. Letters 4, 66 (1960).

⁴ C. D. Clark, P. J. Kemmey, and E. W. J. Mitchell, Discussions Faraday Soc. 31, 96 (1961).

⁵ C. N. Yang, Phys. Rev. 84, 599 (1951).

because it produces displacement concentrations which do not reflect a back reaction.

Irradiations were performed at 77°K as described previously,¹ and optical measurements were made without intervening warmup in a Cary 14R spectrophotometer. It has been shown that defects introduced at 77°K are stable if maintained at that temperature.¹ Electron accelerator energies of 2.0, 1.5, 1.0, and 0.75 MeV were used. These correspond to average electron energies in the sample of 1.85, 1.35, 0.83, and 0.54 MeV. Corrections to the measured absorption coefficients and calculations of the effective electron energy were made as detailed in previous work.³ The ratios of the coefficients at energy E to those at 1.85 MeV, normalized to unity at 1.85 MeV, are plotted in Fig. 1 for the samples taken from crystals grown at the two growth rates investigated.

IV. DISCUSSION

The data shown in Fig. 1 clearly indicate that C -band absorption arising from fast electron irradiation at 77°K is to be associated with displacement of lattice atoms. Since the experimental ratio of the number of defects at successively lower electron energies to that at 1.85 MeV approaches zero, a definite bombarding threshold energy for displacement E_t is indicated. This displacement process must come about as a result of Coulomb encounters of the electron with the lattice atoms. Displacement mechanisms which involve electron excitation⁶ or multiple ionization⁷ cannot play a major role; if they did the data points would follow a stopping-power curve, i.e., the ratio $\alpha(E)/\alpha(1.85 \text{ MeV})$ would increase with decreasing electron energy.

In Fig. 1 the experimental data are plotted against the ratios of the calculated oxygen and silicon displacement cross sections, normalized to unity at 1.85 MeV, for various values of the parameter E_d . If oxygen displacement is responsible for C -band absorption, the data indicate a displacement threshold of 15 ± 5 eV for fast-growth material and 50 ± 5 eV for slow-growth crystals. For silicon displacements one obtains a value of 10 ± 5 eV and 30 ± 5 eV, for the fast and slow growth rates, respectively.

The change in displacement threshold energy with the rate of crystal growth implies that structural imperfections play a major role in determining the number of point defects which can be introduced by electron bombardment. A similar proposal has recently been advanced by Garlick⁸ *et al.* to account for the large

changes in CdS emission for low γ -ray doses. These changes are known to be brought about by a displacement process. Garlick *et al.*, concluded that dislocations and disorder in the crystals were responsible for changes in emission, which were much larger than predicted by the experimental value⁹ of the threshold displacement energy.

Experiments that indicate the importance of the growth rate of quartz on its structural properties are the internal friction measurements of Jones and Brown¹⁰ which were made on synthetic quartz grown at varying rates. These measurements indicated that a 50°K loss maximum increased by two orders of magnitude when the crystal growth rate increased by a factor of four. This internal friction peak was previously associated by Bömmel, Mason, and Warner¹¹ with the motion of nonbridging oxygen atoms.

These considerations suggest that the variation in threshold energy with growth rate is due to consequent variations in crystalline perfection. Incomplete bonding between atoms leads to a decrease in the energy required for displacement.

The data presented do not allow an unambiguous determination of the species that is displaced, i.e., whether it is an oxygen or silicon atom displacement which leads to C -band absorption. One would expect, however, that the displacement of a silicon atom should require more energy than the displacement of an oxygen atom, since the former requires that four bonds be broken whereas the latter requires that two bonds be broken. A value of 30 ± 5 eV for displacement of silicon in slow-growth quartz seems too low, which implies that oxygen displacements are the cause for C -band formation. In addition, the same assignment was previously made by Mitchell and Paige¹² on the basis of optical bleaching of C -band absorption. The value of 50 ± 5 eV for displacement of oxygen in quartz grown slowly and thus, presumably, of higher crystalline perfection seems reasonable for a high-melting-point material, and is consistent with similarly high values for displacement in Al_2O_3 and diamond.

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¹⁰ C. K. Jones and C. S. Brown, Proc. Phys. Soc. (London) **79**, 930 (1962).

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