

Investigations of Oxygen-Defect Interactions between 25 and 700°K in Irradiated Germanium*

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Oxygen impurity atoms interact with radiation-induced defects in germanium over a wide temperature range, producing a variety of optically active oxygen-defect complexes. Two complexes with bands at 719 and 736 cm^{-1} , not present after irradiation at 25°K, develop on annealing between 58 and 73°K in oxygen-doped Ge. One of these complexes is shown by isotopic substitution to contain oxygen and demonstrates conclusively that impurity-defect interactions occur in germanium at low temperatures. A third band at 620 cm^{-1} , which develops near 120°K with the disappearance of the first two bands, is also associated with a complex containing oxygen. By analogy to oxygen-defect interactions in silicon, these complexes are postulated to be oxygen-vacancy complexes, formed as the vacancy moves at $\sim 65^\circ\text{K}$. Many other species develop at temperatures above 273°K. Their annealing behavior indicates that existing complexes react with additional defects or impurity atoms to form new species. Some of the annealing stages occur at temperatures corresponding to annealing stages reported for germanium containing other dopants, suggesting that analogous interactions occur between defects and a variety of impurities.

I. INTRODUCTION

INTERACTIONS between radiation-induced defects and impurity atoms in semiconductors result in the formation of stable complexes which have pronounced effects on the electrical properties of the host material. Well-known examples of such electrically active complexes are the *A* and *E* centers in irradiated Si. These centers have been identified by Corbett, Watkins, and co-workers as oxygen-vacancy¹ and phosphorus-vacancy² complexes, respectively.

The formation of defect-impurity complexes near room temperature in arsenic-doped germanium has been suggested by Brown, Augustyniak, and Waite,³ and evidence for the formation of antimony-defect complexes in germanium near room temperature has also been reported by Pigg and Crawford.⁴ In previous work,⁵ radiation-induced infrared absorption bands in the spectrum of oxygen-doped germanium were attributed to vibrational modes of oxygen-defect complexes which were also formed above room temperature.

Although defect-impurity interactions have been suggested to occur at temperatures as low as 4°K in Si,⁶ evidence for such interactions in germanium at low temperatures is meager. Recent electrical measurements on irradiated As- and Sb-doped germanium, reported by Saito and Pigg,^{7,8} suggest that dopant-defect complex formation occurs between 80 and 180°K.

Since motions only of primary defects are anticipated in this temperature range, the complexes that form are expected to be the simplest types, such as impurity-vacancy or impurity-interstitial complexes. Proof of such interactions and the identification of the associated defects would be useful in characterizing defect motion in germanium.

The determination of the vacancy mobility is of particular interest, since the reported mobilities in Ge differ drastically from those observed in silicon. In Si, vacancy motion has been positively associated with activation energies of ~ 0.1 and 0.33 eV, depending on the charge on the vacancy.⁹ In Ge, the only experimental information for the vacancy migration energy was obtained from self-diffusion, quenching, and annealing studies which yielded values of 1.0–1.2 eV for the activation energy.¹⁰ Recently, Seeger¹¹ suggested that the quenching experiments may have involved the formation of divacancies instead of single vacancies. The divacancy binding energy, which is expected to control the migration of divacancies, has been calculated¹² to be ~ 1.1 eV, which agrees with the activation energies derived from the quenching data and assigned to vacancies. If Seeger's suggestion is correct, then the migration energy of single vacancies would be expected to be much lower than that for divacancies.

The present study of oxygen-defect interactions in germanium was undertaken in an attempt to provide additional insight about defect migration in that material. For this reason, particular emphasis is placed on interactions at low temperatures where the migration

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¹ J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, *Phys. Rev.* **121**, 1015 (1961).

² G. D. Watkins and J. W. Corbett, *Phys. Rev.* **134**, A1359 (1964).

³ W. L. Brown, W. M. Augustyniak, and T. R. Waite, *J. Appl. Phys.* **30**, 1258 (1959).

⁴ J. C. Pigg and J. H. Crawford, Jr., *Phys. Rev.* **135**, A1141 (1964).

⁵ R. E. Whan and H. J. Stein, *Appl. Phys. Letters* **3**, 187 (1963); *R. E. Whan, Bull. Am. Phys. Soc.* **9**, 278 (1964); **10**, 320 (1965).

⁶ G. D. Watkins, *Bull. Am. Phys. Soc.* **9**, 48 (1964).

⁷ H. Saito and J. C. Pigg, *Bull. Am. Phys. Soc.* **9**, 654 (1964).

⁸ J. C. Pigg (private communication).

⁹ G. D. Watkins, *Proceedings of the 7th International Conference on the Physics of Semiconductors: Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, p. 97.

¹⁰ A. Hiraki and T. Suita, *J. Phys. Soc. Japan* **18**, Suppl. III, 254 (1963), and references contained therein.

¹¹ W. L. Brown, in *Proceedings of the 7th International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 1313.

¹² A. Scholz and A. Seeger, *Proceedings of the 7th International Conference on the Physics of Semiconductors: Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), Vol. 3, p. 315.

of primary defects is anticipated. Annealing studies at higher temperatures provide additional information on more complicated processes, involving the migration of secondary defects and impurity atoms.

II. EXPERIMENTAL

A. Measurements

Optical-absorption spectra were recorded with either a Beckman IR-7 spectrophotometer (4000–650 cm^{-1}) or with a Beckman IR-9 spectrophotometer (4000–400 cm^{-1}). Room-temperature spectra were recorded using a cryostat base designed especially to fit the beam condenser. For spectra recorded during isochronal annealing studies in which the absorption bands developed only to low intensities, a wide slit ($\sim 2 \text{ cm}^{-1}$), slow scan, and long integration time were used to increase the signal-to-noise ratio.

B. Irradiation Apparatus

All irradiations were performed using 2-MeV electrons. The 25 and 80°K irradiations were carried out in vacuum using a standard cryostat. The rotatable base of the cryostat possessed four ports, two of which were equipped with NaCl or KBr windows for optical measurements. One of the ports at right angles to these was equipped with an aluminum Faraday cage. The fourth port held an aluminum cup insert with 0.003-in. thick window located only $\frac{1}{2}$ in. from the sample. The end of the Van de Graaff accelerator tube was equipped with a mating cup which fitted snugly into this insert. This arrangement facilitated interruptions of the irradiation for optical measurements and minimized the loss of beam intensity from small-angle scattering.

The sample was mounted in an indentation in a copper sample block and soldered in place with indium. A thermocouple was attached with indium solder to the sample edge. Sliding frames, covered with 2-mil copper foil, were mounted on the sample block and prevented condensation on the sample surface during irradiation. The foil doors were moved out of the optical path during measurements. An insulated aluminum mask, with a beam-defining aperture of 0.23×0.48 in., was mounted on the heat shield directly in front of the sample and collimated the beam. The beam was scanned electromagnetically over the sample. Electrical leads connected the insulated sample block and the rear Faraday cup to an Elcor model A209A current integrator. For the 25°K irradiation, liquid helium was used as the coolant. The sample temperature was maintained below 25°K with a beam current of 2 μA striking the sample. For the 80°K irradiation, pumped liquid nitrogen was used, and the sample temperature remained below 80°K with a 2- μA beam current.

The 20 and 60°C irradiations were performed in air with the sample mounted on a water-cooled holder. Additional cooling was provided by eight cold nitrogen

gas jets directed at sample surfaces. A thermocouple was wedged against the front surface of the sample. The electron beam was similarly scanned, collimated to 0.25×0.25 in., and integrated by the current integrator. The temperature at the sample surface was maintained within 2 degrees of the selected temperature by controlling the cold N_2 flow and adjusting the beam current.

C. Sample Preparation

All oxygen-doped germanium samples were obtained from Semi-Elements, Inc. The samples doped with naturally occurring oxygen (99.76% O^{16}) were cut from the same ingot of single-crystal germanium and were all about the same size ($0.25 \times 0.25 \times 0.10$ in.). The material, as grown, displayed an absorption band at 856 cm^{-1} at room temperature associated with a germanium-interstitial oxygen complex. Using the data of Kaiser¹³ relating the intensity of this absorption band to the concentration of the interstitial complex, a concentration of 2.7×10^{17} complexes/ cm^3 was determined for this sample. A much weaker band at 785 cm^{-1} , identified by Kaiser¹³ as belonging to a GeO_4 aggregate, was also present. The low resistivity of the material, 0.08 $\Omega \text{ cm}$, was undoubtedly due to the presence of that species which has donor characteristics. Heat treatment of a sample at 915°C in a quartz tube under 10 mm air pressure for 2 min followed by rapid quenching to room temperature (15 sec) caused the GeO_4 band to disappear, and the resistivity increased to 2 $\Omega \text{ cm}$. The germanium-interstitial oxygen band at 856 cm^{-1} indicated the concentration to be 5.7×10^{17} complexes/ cm^3 after heat treatment. Heat treatment of a sample at 530°C for 30 min increased the resistivity to 0.8 $\Omega \text{ cm}$. Samples of germanium doped with oxygen, enriched with 65% O^{18} , were used without heat treatment. The total oxygen concentration in this material was about 1×10^{17} atoms/ cm^3 .

III. RESULTS

A. Low-Temperature Irradiation and Annealing

An electron irradiation of oxygen-doped germanium was performed at 25°K to $\Phi = 4 \times 10^{17} \text{ e/cm}^2$ to determine if any new or previously reported⁵ oxygen-defect complexes were formed at low temperatures. No absorption bands were introduced into the spectrum by the irradiation (curves A and B, Fig. 1). The sample was annealed isochronally in 15°K increments for 10 min at each temperature. No new bands were detectable in the sample after annealing up to 58°K (curve C, Fig. 1). Annealing at 73°K, however, produced absorption bands at 719 and 736 cm^{-1} (curve D, Fig. 1). The intensities of these bands increased slightly upon annealing at 88°K. The growth curves for the two bands are shown in Fig. 2.

¹³ W. Kaiser, J. Phys. Chem. Solids 23, 255 (1962).

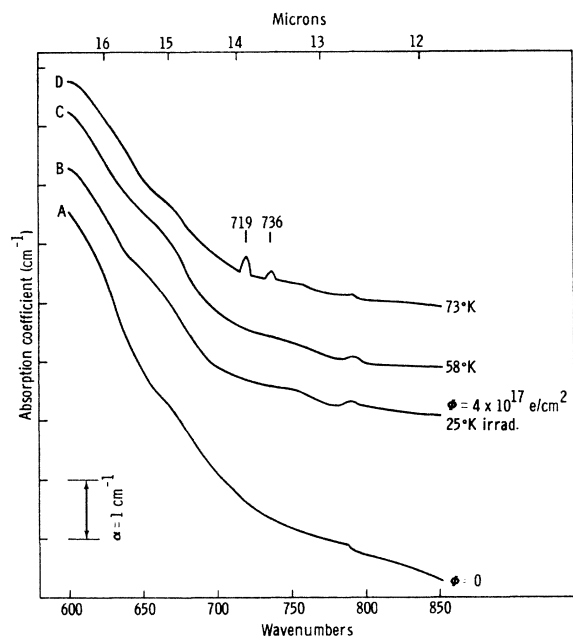


FIG. 1. Infrared spectra of oxygen-doped germanium. Spectra have been vertically displaced for clarity. All spectra recorded at 10°K. A. Pre-irradiation. B. After 25°K irradiation to $\Phi = 4 \times 10^{17}$ e/cm². C. After 10-min anneal at 58°K. D. After 10-min anneal at 73°K.

Two other samples, one oxygen-doped and one oxygen-free, were irradiated at 80°K to $\Phi = 6 \times 10^{17}$ e/cm². The spectra of the oxygen-doped sample before and after the irradiation are shown by curves A and B in Fig. 3. The pair of bands at 719 and 736 cm⁻¹, present in the post-irradiation spectrum, is the same pair produced by the annealing of the 25°K irradiated sample as described above. The irradiation and annealing of the oxygen-free sample does not produce any of the absorption bands reported in this paper.

Annealing of the irradiated oxygen-doped sample to 148°K results in the disappearance of both the 719- and 736-cm⁻¹ bands and abrupt growth of a new species at 620-cm⁻¹ (spectra C and D of Fig. 3). Annealing up to

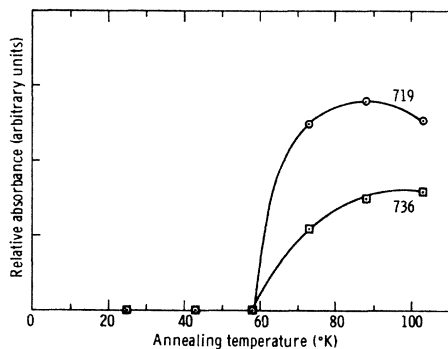


FIG. 2. Isochronal annealing curves for growth of absorption bands appearing in low temperature range. Sample irradiated at 25°K to $\Phi = 4 \times 10^{17}$ e/cm².

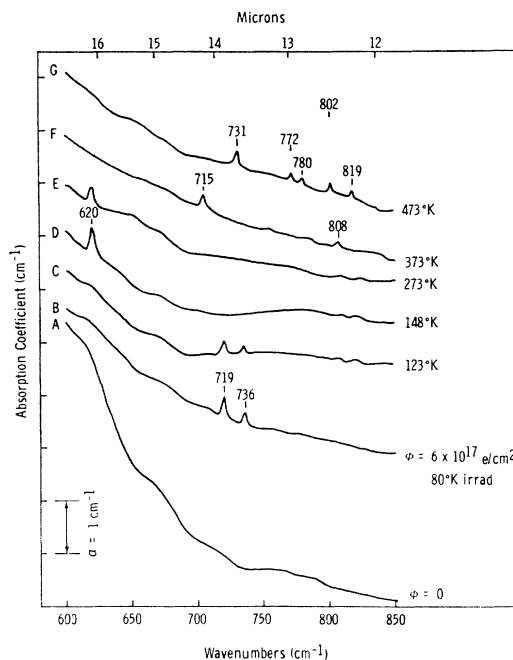


FIG. 3. Infrared spectra of oxygen-doped germanium. Spectra have been vertically displaced for clarity. All spectra recorded at 80°K. A. Pre-irradiation. B. After 80°K irradiation to $\Phi = 6 \times 10^{17}$ e/cm². C. After 20-min anneal at 123°K. D. After 20-min anneal at 148°K. E. After 20-min anneal at 273°K. F. After 20-min anneal at 373°K. G. After 20-min anneal at 473°K.

248°K results in a small decrease in the intensity of the 620-cm⁻¹ band. Annealing above this temperature causes the band to decay (curve E, Fig. 3). After the 373°K anneal, the 620-cm⁻¹ band is completely decayed and two other bands at 715 and 808 cm⁻¹ have appeared (curve F, Fig. 3). Annealing at higher temperatures develops five more bands as shown by curve G in Fig. 3. The bands which developed at the higher temperatures have been observed previously⁵ in the room-temperature spectrum of a sample irradiated at 333°K. The frequencies of the bands are ~ 5 cm⁻¹ lower in the spectra measured at room temperature than in those measured at 80°K.

Annealing curves for the bands formed at low and at high temperatures are shown in Figs. 4 and 5, respectively. Seven temperature ranges in which reordering processes occur have been designated on the graphs.

Range I at ~ 120 °K (or about -150 °C) includes the decay of the two bands at 719 and 736 cm⁻¹ present immediately after the 80°K irradiation and the growth of the 620-cm⁻¹ species. Range II, 0 to 50°C, is characterized by the decay of the 620-cm⁻¹ band and the growth of two bands at 808 and 715 cm⁻¹. The latter bands grow at approximately the same rate and begin to decay at 100 to 125°C (range III). Also in range III, two more bands, 802 and 731 cm⁻¹, start to develop. The band at 802 cm⁻¹ reaches a maximum intensity and begins to decay in range IV, 175 to 200°C. Range IV also includes the appearance of bands at 772 and 780 cm⁻¹.

An additional band at 819 cm^{-1} develops throughout both range III and IV. Between 200 and 225°C , range V, the three bands at 731 , 772 , and 819 cm^{-1} start to decay.

The band at 780 cm^{-1} , which reaches an intensity plateau between 175 and 250°C , begins to grow again at 250°C , range VI. Finally, in range VIII, 325 to 350°C , the 780-cm^{-1} band decays and a band at 789 cm^{-1} (not shown), identified by Kaiser¹⁸ as a GeO_4 aggregate, appears. This latter species is formed at the same temperatures in unirradiated samples. Annealing at higher temperatures does not develop additional bands.

B. Isotopic Shifts in Radiation-Induced Absorption Bands

The large number of radiation-induced bands present in the spectrum of oxygen-doped germanium must originate from a variety of complexes. These complexes probably consist of combinations of one or more defects associated with one or more impurity atoms. The species formed at the lower temperatures are expected to be the simplest types. By studying the isotope shift in the frequencies of the bands in the spectrum of germanium doped with oxygen enriched with O^{18} , the presence of oxygen atoms in some of the complexes can be established.

In ordinary oxygen-doped germanium it was found that the irradiation temperature had a pronounced effect on the intensities of the various bands. Consequently, several irradiations at different selected temperatures were performed on samples doped with oxygen enriched with O^{18} , in order to develop particular bands to their maximum intensities. Even under optimum experimental conditions, however, some of the spectral bands did not develop to detectable intensities, and others were very weak. The nonappearance of the radiation-induced bands generally prominent in the spectra of samples doped with ordinary oxygen may result from one of several factors. The oxygen content

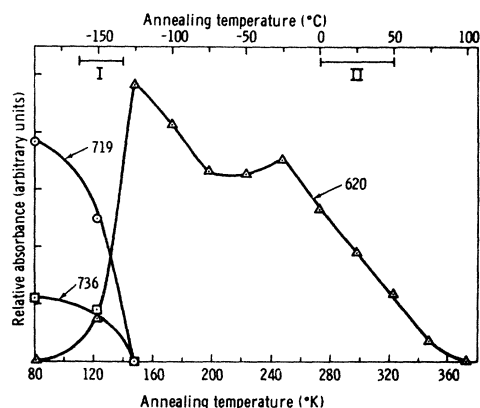


FIG. 4. Isochronal annealing curves for absorption bands appearing in low-temperature annealing range. Sample irradiated at 80°K to $\Phi = 6 \times 10^{17}\text{ e/cm}^2$.

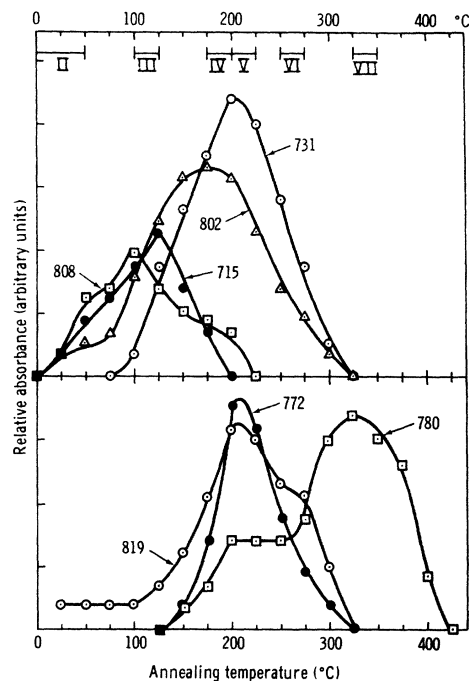


FIG. 5. Isochronal annealing curves for absorption bands appearing in high-temperature annealing range. Sample irradiated at 80°K to $\Phi = 6 \times 10^{17}\text{ e/cm}^2$.

of the O^{18} -enriched samples may be too low for some complexes to be formed in detectable concentrations, or some of the complexes may involve other impurity atoms whose concentrations are too low in the O^{18} .

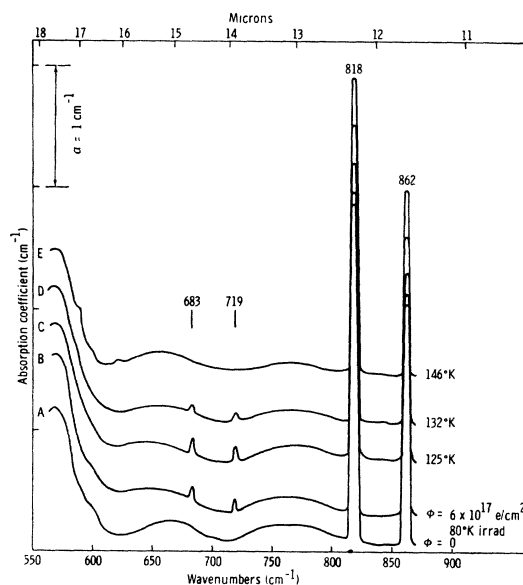


FIG. 6. Infrared spectra of germanium doped with oxygen enriched with $65\% \text{O}^{18}$. All spectra recorded at 80°K . Spectra have been vertically displaced for clarity. A. Pre-irradiation. B. After 80°K irradiation to $\Phi = 6 \times 10^{17}\text{ e/cm}^2$. C. After 10-min anneal at 125°K . D. After 10-min anneal at 132°K . E. After 10-min anneal at 146°K .

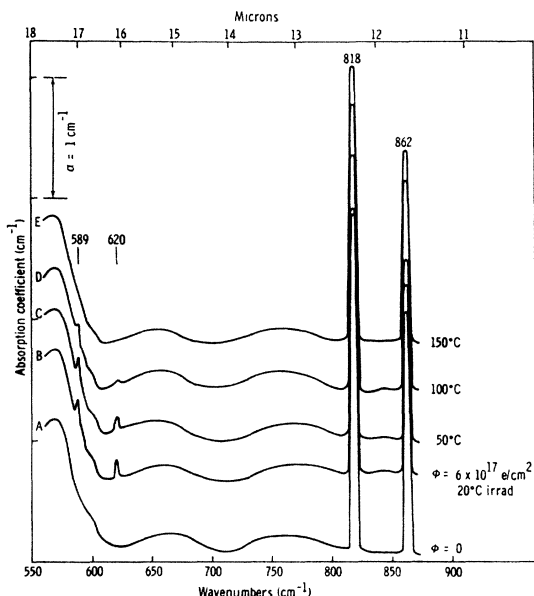


FIG. 7. Infrared spectra of germanium doped with oxygen enriched with 65% O^{18} . All spectra recorded at 80°K. Spectra have been vertically displaced for clarity. A. Pre-irradiation. B. After 20°C irradiation to $\Phi=6 \times 10^{17} e/cm^2$. C. After 20-min anneal at 50°C. D. After 20-min anneal at 100°C. E. After 20-min anneal at 150°C.

enriched samples for the formation of the corresponding complexes in detectable concentrations. Another possibility is that the Fermi level of the sample may be too low for some of the complexes to be stable.

The low-temperature absorption spectrum of an un-irradiated sample of germanium doped with oxygen enriched with 65% O^{18} is shown by curve A in Fig. 6. The sample possesses absorption bands at 862 and 818 cm^{-1} . The band at 862 cm^{-1} is also found in O^{16} -doped germanium and is associated with the germanium-interstitial O^{16} complex. The band at 818 cm^{-1} appears only in samples containing O^{18} and must be associated with the analogous germanium-interstitial O^{18} complex. Curve B in Fig. 6 represents the spectrum of the sample after irradiation at 80°K to $\Phi=6 \times 10^{17} e/cm^2$. The band at 719 cm^{-1} is present as expected and an additional band at 683 cm^{-1} has developed. Annealing between 125 and 146°K causes the pair of bands to decay together (curves C, D, E, Fig. 6).

The low-temperature spectrum of a sample after electron irradiation at 20°C to $\Phi=6 \times 10^{17} e/cm^2$ is shown by curve B in Fig. 7. Two prominent radiation-induced bands are present, one at 620 cm^{-1} observed previously in the spectrum of irradiated O^{16} -doped germanium and a new band at 589 cm^{-1} . Annealing of the sample up to 150°C results in the simultaneous disappearance of the two bands. This behavior is demonstrated by curves C, D, and E. Annealing at higher temperatures did not produce any additional bands in the spectrum.

Another sample was irradiated at 60°C to $\Phi=6 \times 10^{17} e/cm^2$. The low-temperature spectrum after irradiation is shown by curve B in Fig. 8. Two bands, one at 731 cm^{-1} also observed in the spectrum of irradiated O^{16} -doped germanium and a new one at 694 cm^{-1} , are prominent. These bands also decay together upon annealing at elevated temperatures, as shown by curves C and D.

Continued annealing of this sample develops simultaneously three weak bands, 780, 757, and 739 cm^{-1} in the spectrum of the sample. Heating above 300°C causes the three bands to anneal out together as seen in curve F. No other discernible bands developed during the irradiation at 60°C or subsequent annealing.

IV. DISCUSSION

A. Determination of Composition by Isotopic Substitution

The substitution of an isotopic atom for a different isotope of the same element in a molecule results in a vibrational frequency shift because of the change in mass. Thus isotopic substitution of O^{18} for O^{16} in oxygen-doped germanium makes it possible to establish that at least four of the radiation-induced bands are vibrational modes of defect-oxygen complexes.

The valence-force approximation¹⁴ yields the following expression for the vibrational frequency of the interstitial oxygen-germanium complex.

$$(2\pi\nu)^2 = [1 + (2M_{Ge} \sin^2\alpha)/M_O]k/M_{Ge}, \quad (1)$$

where k is the force constant between Ge-O, 2α is the angle formed by the Ge-O-Ge species, M_O is the oxygen mass, and M_{Ge} is the effective germanium mass. By substituting O^{18} for O^{16} , only the oxygen mass is expected to change. The square of the frequency ratio for the isotope shift is given by

$$\left[\frac{\nu_{O^{18}}}{\nu_{O^{16}}}\right]^2 = \left[\frac{M_{O^{16}} + 2M_{Ge} \sin^2\alpha}{M_{O^{18}} + 2M_{Ge} \sin^2\alpha}\right] \left[\frac{M_{O^{18}}}{M_{O^{16}}}\right]. \quad (2)$$

Values near unity are expected for the quantity containing the germanium mass since, for reasonable values of α , the term $2M_{Ge} \sin^2\alpha$ is the dominant one in the expression. Thus, the square of the frequency ratio is expected to be approximately equal to the ratio of the oxygen masses. Analogous expressions can be derived for oxygen-defect complexes with different configurations. These can be simplified in much the same manner since the mass of germanium is much larger than that of oxygen. Thus for most of the complexes the relationship,

$$[\nu_{O^{18}}/\nu_{O^{16}}]^2 \approx [M_{O^{18}}/M_{O^{16}}],$$

¹⁴ G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945), pp. 168 ff. and 228 ff.

is expected to hold, where $\nu_{O^{18}}$ refers to the vibrational frequency of the totally O^{18} -substituted complex.

For complexes containing more than one oxygen atom, mixed species containing both O^{16} and O^{18} atoms are possible in a crystal doped with both of the isotopes. The effect of the partial isotopic substitution on a given vibrational mode of such a multi-oxygen complex depends on its configuration and bonding. If the oxygen atoms vibrate independently of each other, a particular vibrational mode will be associated with only two absorption bands corresponding to the independent O^{16} and O^{18} vibrations. If the oxygen atoms are coupled to each other, then band broadening or the appearance of more than two bands is expected.

The square of the ratio of the frequencies of the bands corresponding to the germanium-interstitial O^{16} complex and the analogous O^{18} complex (curve A, Fig. 6) is $(862/818)^2 = 1.11$. This is approximately equal to the ratio of the oxygen masses ($M_{O^{18}}/M_{O^{16}} = 1.125$) as expected.

The irradiation at 80°K was expected to produce the 719-cm^{-1} band and an isotopic analog at a lower frequency. Since this complex is formed at the lowest temperatures, where only primary defects are expected to move, it is expected to be a relatively simple species, probably containing only one oxygen atom. Irradiations at higher temperatures were expected to produce more complicated species which could contain more than one oxygen atom or associated defect.

The 80°K irradiation of germanium doped with the mixed isotopes produced a pair of bands, 719 and 683 cm^{-1} , as expected, which annealed out together (Fig. 6). The band at 683 cm^{-1} did not appear in the spectrum of irradiated germanium doped with ordinary oxygen (Fig. 3). The square of the frequency ratio is $(719/683)^2 = 1.11$, the same as the square of the ratio for the interstitial bands. These results establish that the pair of bands are associated with isotopic analogs of an oxygen-defect complex. The 719-cm^{-1} band belongs to a vibrational mode of the O^{16} complex and the 683-cm^{-1} band to the mode of the analogous O^{18} complex. The sharpness of these two bands and lack of structure between them suggests the complex probably contains only one oxygen atom.

The square of the ratio of frequencies of the pair of bands present immediately after the 20°C irradiation (Fig. 7) is $(620/589)^2 = 1.11$, the same as the square of the frequency ratio for the interstitial bands. This evidence, the presence of the 589-cm^{-1} band only in the spectra of O^{18} -enriched samples, and the identical annealing behavior of the two bands establish that they originate from the same type of complex. The higher frequency band is associated with the O^{16} -defect complex, and the band at 589 cm^{-1} is associated with the analogous O^{18} complex. The bands are sharp with no detectable side structure, suggesting that this complex also contains only one oxygen.

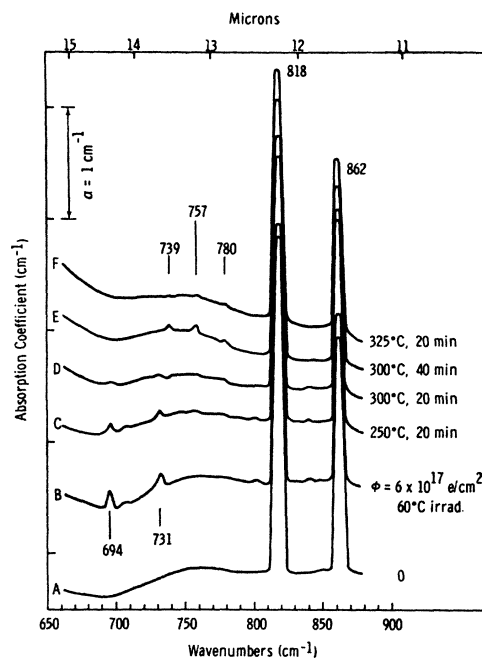


Fig. 8. Infrared spectra of germanium doped with oxygen enriched with 65% O^{18} . All spectra recorded at 80°K . Spectra have been vertically displaced for clarity. A. Pre-irradiation. B. After 60°C electron irradiation to $\Phi = 6 \times 10^{17} \text{ e/cm}^2$. C. After 20-min anneal at 250°C . D. After 20-min anneal at 300°C . E. After 40-min anneal at 300°C . F. After 20-min anneal at 325°C .

The two bands produced by irradiation at 60°C display a similar relationship (Fig. 8). The square of their frequency ratio is $(731/694)^2 = 1.11$, which is also equal to that of the interstitial bands. The simultaneous decay of the bands upon annealing and appearance of the lower frequency band only in spectra of O^{18} -containing samples establish that the bands originate from isotopic analogs of the same complex.

For the three bands which developed simultaneously in the spectrum after the 300°C anneal, the squares of the frequency ratio are $(780/739)^2 = 1.11$ and $(780/757)^2 = 1.06$. The former is also approximately equal to $(M_{O^{18}}/M_{O^{16}})$. The latter is approximately $17/16 = 1.062$, suggesting a partially substituted species containing more than one oxygen. The identical annealing properties of the three bands and the presence of the two lower frequency bands only in spectra of O^{18} -enriched samples establish that they originate from the same type of complex. The fact that there are more than two bands indicates the associated complex contains more than one oxygen atom. The 780-cm^{-1} band corresponds to a complex containing only O^{16} atoms, the 739-cm^{-1} band to a complex containing only O^{18} atoms, and the 757-cm^{-1} band to the mixed species containing both O^{16} and O^{18} atoms.

B. Annealing

The results of the 25 and 80°K irradiations and subsequent annealing combined with the results of the iso-

tope doping in the foregoing section demonstrate defect-impurity interaction over a wide temperature range. The results can be compared to observations in oxygen-doped silicon to yield information about the nature of the complexes and the mechanisms of their formation. The annealing stages observed in the present studies can also be related to observations published by other workers for *n*-type germanium. For convenience, the discussion is separated into two parts, annealing below 273°K where primary defect migration is expected to occur, and annealing above 273°K where complex reordering processes are anticipated.

1. Annealing below 273°K

The absorption bands at 719 and 736 cm⁻¹, undetectable after a 25°K irradiation, developed together upon annealing at 73°K (Fig. 1). The 719-cm⁻¹ band is shown to be associated with a complex which contains oxygen. Although the species with the band at 736 cm⁻¹ has not been positively identified as an oxygen-containing complex, the fact that it is not detected in irradiated oxygen-free samples suggests that it does contain oxygen. Since the annealing temperature is too low for the diffusion of oxygen to occur, the complex-forming defect must begin to migrate between 58 and 73°K. This motion probably corresponds to the 65°K annealing stage reported by Klontz and MacKay¹⁵ for *n*-type germanium. They estimated that this stage is associated with an activation energy of ~0.2 eV. This value is on the order of that reported by Watkins⁹ for vacancy migration in *p*- or *n*-type silicon (0.33 or ~0.1 eV, respectively).

The fraction of radiation-induced defects which are trapped by the oxygen atoms in this stage can be estimated from the total irradiation dose and the intensities of the bands at 719 and 736 cm⁻¹. The average defect production rate for 2-MeV electrons is on the order of two displacements per incident electron.¹⁶ If it is assumed that the oscillator strengths for the vibrational transitions for the oxygen-defect complexes are approximately equal to that for the interstitial oxygen complex, the concentrations of the oxygen-defect complexes can be estimated from Kaiser's data which relate the absorption coefficient to the concentration of interstitial oxygen complexes. While this assumption is rather tenuous, it probably yields the correct order of magnitude. Thus, using these approximations we find that only a small percent, ~0.5%, of the defects react with oxygen to form these complexes. This is consistent with the results for irradiated degenerate *n*-type Ge, reported by Klontz and MacKay,¹⁵ which show that a large percentage of the damage anneals at 65°K. They attribute this recovery to recombination of close vacancy-interstitial pairs.

The bands at 719 and 736 cm⁻¹ are also produced during the irradiation at 80°K as expected from their growth curves in Fig. 2. Their decay between 110 and 130°K is accompanied by the rapid development of the 620-cm⁻¹ species which also contains oxygen as shown above. The latter complex is relatively stable over a wide temperature range (Fig. 4). A spin-resonance signal observed in irradiated oxygen-doped germanium has been identified as a resonance associated with the germanium *A* center or negatively charged oxygen-vacancy pair.¹⁷ A comparison of the annealing of the 620-cm⁻¹ band with the annealing of this resonance reveals that they both decay in the same temperature range, suggesting that the 620-cm⁻¹ band is associated with the *A* center.

The vibrational frequency for the germanium *A* center can be estimated in the following manner. In Si, since the frequency ratio for isotopic analogs of the interstitial oxygen complex is approximately equal to the frequency ratio of the isotopic analogs of the oxygen-vacancy complex, Corbett and co-workers¹ concluded that the bond angles for the two types of complexes are approximately equal. Corbett *et al.* then concluded that the ratio of the force constant of the oxygen-vacancy complex to that of the interstitial oxygen complex is primarily a function of the bond distances. Since the bond distances and configurations in silicon and germanium should be almost equivalent, let us assume the same relationships hold in germanium. Then,

$$[\nu_v/\nu_i]_{\text{Ge}} \approx [k_v/k_i]_{\text{Ge}} \text{ or } \text{Si} \approx [\nu_v/\nu_i]_{\text{Si}}^2,$$

where *v* and *i* refer to vacancy-oxygen and interstitial oxygen complexes, respectively. Substitution of the known frequencies in this expression yields the value

$$(\nu_v)_{\text{Ge}} \approx 630 \text{ cm}^{-1},$$

which is close to the frequency of the 620-cm⁻¹ band. The low formation temperature and stability of the 620-cm⁻¹ species, the presence of oxygen in the complex, the agreement in annealing behaviors for the 620-cm⁻¹ band and the Ge *A*-center resonance, and the agreement in the observed and predicted frequencies all lead to the assignment of the 620-cm⁻¹ band to the negatively charged oxygen-vacancy complex.

The simultaneous growth of the 620-cm⁻¹ band and decay of the 719- and 736-cm⁻¹ bands suggest the species are related. As pointed out earlier,¹⁸ a possible explanation is that the species differ in charge or spatial configuration. An almost analogous behavior in the spin resonance of irradiated *n*-type oxygen-doped silicon has been reported.⁹ Upon annealing, the resonance of the negatively charged vacancy decayed at ~60°K. Two other resonances grew in and decayed with increasing temperature before the Si *A*-center resonance appeared at 120°K. Watkins has suggested that the two resonances

¹⁵ E. E. Klontz and J. W. MacKay, *J. Phys. Soc. Japan* **18**, Suppl. III, 216 (1963).

¹⁶ J. H. Cahn, *J. Appl. Phys.* **30**, 1310 (1959).

¹⁷ J. A. Baldwin, *J. Appl. Phys.* **36**, 793 (1965).

¹⁸ R. E. Whan, *Appl. Phys. Letters* **6**, 221 (1965).

which develop prior to the *A*-center resonance are associated with "excited configurations" of oxygen-vacancy complexes.¹⁹ The present results suggest such species are also formed in the same temperature range in germanium.

Thus a comparison of the low-temperature annealing behaviors for irradiated oxygen-doped germanium and silicon reveals striking similarities. In silicon, the motion of negatively charged vacancies begins at 60°K and is associated with an estimated activation energy of 0.1 eV. This motion results in the formation of complexes which undergo modification with increasing temperatures, finally resulting in the formation of the *A* center at 120°K. In germanium, defect motion resulting in the formation of complexes shown to contain oxygen occurs between 58 and 73°K with an estimated activation energy of ~0.2 eV. These complexes begin to decay at 120°K as the band associated with the germanium *A* center develops. The analogous behavior in the two materials leads to the conclusion that in Ge the defect which begins to migrate between 58 and 73°K is the negatively charged vacancy.

2. Annealing above 273°K

In contrast to annealing at low temperatures which resulted in the formation of only a few simple complexes, annealing above 273°K produces a manifold of species. Many more vibrational bands are observed in this system than can be accounted for by the limited number of conceivable simple complexes. Processes involving the addition of simple defects, defect aggregates, impurity atoms, or even defect-impurity complexes to existing complexes must occur to produce a variety of more complicated species. In spite of the complexity of the system, two facts become apparent. Certain species are produced from modification of existing complexes, and some of the annealing stages observed in this system occur at temperatures corresponding to annealing stages in germanium doped with different impurities.

The annealing curve for the 620-cm⁻¹ band in Fig. 4 shows the gradual disappearance of the species over a large temperature range beginning at about 0°C. The shape of the curve is not characteristic of a thermal dissociation. It suggests that the species is undergoing alteration by complexing with additional reactants. The growth of two more bands, 808 and 715 cm⁻¹ (Fig. 5), in the same temperature range tends to substantiate this observation.

Brown and co-workers³ reported that an annealing stage for As-doped Ge irradiated at 79°K also occurred in this temperature range with the resultant formation of an As-defect complex. Pigg and Crawford⁴ observed an annealing stage at +25°C in Sb-doped Ge after γ irradiation at 77°K. The agreement in annealing behavior suggests analogous processes are occurring in the

O-, As-, and Sb-doped samples. Pigg and Crawford suggest that the annealing stage might correspond to the migration of single vacancies with the resultant formation of vacancy-dopant complexes. The present results indicate that the new complexes are formed in this stage from the reaction of a defect or impurity atom with existing complexes.

The next annealing stage occurs in range III, 100 to 125°C, where the growth of two bands is accompanied by the decay of the two bands formed in range II. One of the new bands (731 cm⁻¹) is shown in the preceding section to be associated with a complex also containing oxygen. The simultaneous growth and decay of these bands suggests that the two new species are formed directly from the decaying species or from their dissociation products.

Pigg and Crawford⁴ also observed an annealing stage at 100°C in Sb-doped germanium and found that the ratio of recovery for their first two stages (25 and 100°C) showed a marked dependence on the Sb concentration. They suggested that antimony-vacancy complexes, formed in the 25°C stage, thermally dissociate in the 100°C stage. The freed vacancies interact with still-existing Sb-vacancy complexes to form Sb-divacancy complexes. The apparent activation energy for the process at low temperatures (<150°C) was found to be 1.2 eV.

There is also the strong possibility that this annealing stage is associated with divacancy migration. The activation energy of this stage, 1.2 eV, is approximately equal to the binding energy for divacancies, calculated by Scholz and Seeger,¹² which is expected to control the migration process. This activation energy is also close to the activation energy of 1.3 eV for divacancy migration in Si reported by Watkins and Corbett.²⁰

Pigg and Crawford⁴ report that an additional species with an energy level at $E_c - 0.09$ eV develops between 80 and 105°C and does not anneal throughout the temperature range studied (to 182°C). The concentration of the species does not display a dependence on the Sb concentration; however, it increases when the sample has received heat treatment in air prior to irradiation. The authors tentatively conclude that this species is an oxygen-defect complex. The annealing behavior of the species suggests that it corresponds to one of the bands which develops in range III (Fig. 5).

The band at 819 cm⁻¹, which develops throughout ranges III and IV, also appears weakly but persistently in the spectra of heat-treated unirradiated oxygen-doped germanium samples but not in the spectra of oxygen-free samples. These results suggest that the band originates from a relatively simple species which can be formed thermally, perhaps a defect-di-oxygen complex or a complex containing oxygen and a different impurity atom.

¹⁹ G. D. Watkins (private communication).

²⁰ G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).

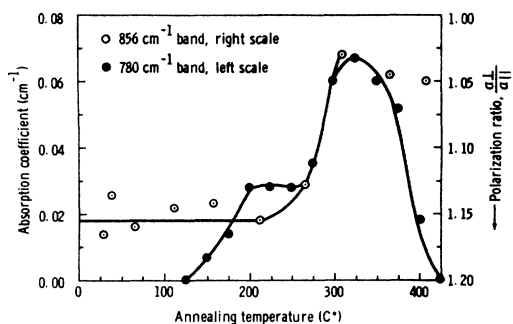


FIG. 9. Comparison of the annealing curve for the radiation-induced band at 780 cm^{-1} with the relaxation of the stress-induced dichroism of the interstitial oxygen band at 856 cm^{-1} taken from Corbett, MacDonald, and Watkins (Ref. 21).

The decay of the three bands, 731 , 772 , and 819 cm^{-1} , in range V at approximately the same rate suggests two possible mechanisms. The three species may be undergoing thermal dissociation, implying the binding energies are very similar. An alternative mechanism is the reaction of all three with a species which begins to migrate in that temperature range, possibly interstitial oxygen. The annealing temperature, however, seems somewhat low for the diffusion of oxygen to be important.

The band at 780 cm^{-1} , shown to be associated with a complex containing at least two oxygen atoms, grows rapidly between 250 and 325°C , range VI. Corbett, McDonald, and Watkins²¹ have shown by studying the relaxation of stress-induced dichroism of the interstitial oxygen band in germanium that interstitial oxygen begins to migrate in that temperature range. A comparison of their relaxation curve and the growth curve for the 780-cm^{-1} band is shown in Fig. 9. The agreement suggests that the formation of the species associated with the 780-cm^{-1} band results from the diffusion of oxygen atoms to existing defects or complexes already containing oxygen. The relaxation of the dichroism, however, involves only one jump by an oxygen atom in contrast to the presumably many jumps required for a dispersed atom to reach and react with a stationary

²¹ J. W. Corbett, R. S. McDonald, and G. D. Watkins, *J. Phys. Chem. Solids* **25**, 873 (1964).

complex. Using their data to determine the jump frequency of the interstitial oxygen at the various annealing temperatures, a total of about 150 jumps per atom is expected during the growth of the 780-cm^{-1} band. Considering the oxygen concentration is approximately one atom in 10^6 , the number of jumps per atom seems somewhat low to account for the rapid growth of the species unless either the oxygen is not dispersed homogeneously throughout the sample or there is a long-range attractive force between the existing complexes and interstitial oxygen. At $\sim 350^\circ\text{C}$ in both irradiated and nonirradiated samples, the band at 785 cm^{-1} associated with a GeO_4 aggregate begins to develop, suggesting that indeed the oxygen is not dispersed uniformly.

The high-temperature annealing properties of irradiated oxygen-doped germanium can be compared with those reported for oxygen-doped silicon.²² In both materials, many infrared bands, associated with oxygen-defect complexes, develop successively over a wide temperature range. With increasing temperatures, the complexes become progressively more complicated, involving oxygen aggregates. In both cases a possible mechanism for the formation of the defect-oxygen aggregate species at higher temperatures is the diffusion of interstitial oxygen to existing complexes. For processes occurring between 250 and 450°C in Si, Corbett and co-workers²² suggested a mechanism involving vacancy-enhanced diffusion of oxygen to stationary interstitial atoms. Although the identities and mechanisms for the formation of the complexes formed at high temperatures are only tentative, there is no question that the processes occurring in both oxygen-doped silicon and germanium are similar not only for the low-temperature range but also for the high-temperature range.

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²² J. W. Corbett, G. D. Watkins, and R. S. McDonald, *Phys. Rev.* **135**, A1381 (1964).