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Temperature Variation of Optical Absorption Band Produced by Oxygen in Silicon Crystal

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Temperature dependency of the 9.0μ absorption band due to oxygen in the silicon single crystal pulled from the silica crucible has been measured in the temperature range 300°K～80°K. This absorption band splits into two peaks at the temperature lower than 125°K. Energy of peak positions, that is the energy of oscillators, are 0.1394eV and 0.1405eV, respectively. The oxygen has two kinds of equilibrium positions around the $\langle 111\rangle$ axis in crystal, and these minimum positions are slightly different each other. The difference of potential energy between these two minimum positions is *ca.* 8×10^{-3}eV, and this value varies with samples which were made under different conditions. Further, electrical properties of these crystals have been measured. According to these experimental results, the difference of energy between these minimum energy points seems to originate from the local distortion around oxygen atom in the silicon crystal.

1. Introduction

As is well known, the silicon single crystal pulled from a silica crucible contains a great amount of oxygen. The solutions of oxygen in these silicon crystal, when subjected to heating at 400～1000°C, undergo changes both in electrical properties and in infrared absorption. Many works in this field have been reported.1)～7) Especially, during recent years the studies on the position of oxygen in silicon crystal have attracted much attention.8)～11) According to those works, these oxygen atoms occupy the interstitial positions rather than the substitutional positions. Recently, the electron spin resonance study also has shown that the oxygen position is interstitial.9),11) That is to say, the oxygen atom dissolved in a silicon crystal forms chemical bonds with two silicon atoms which originally were linked by a covalent bond, and they form a nonlinear (triangle) Si-O-Si molecule imbedded in the silicon lattice. The configuration of the Si-O-Si molecule for interstitial position is shown in Fig. 1. On the other hand, the optical absorption bands of these Si_2O molecules have long been studied.2),3),4),9),12) Up to now three absorption bands were found as shown in Fig. 2. These absorption bands correspond to three vibrational modes of Si_2O molecule imbedded into silicon crystal.12) (cf. Fig. 1.) The properties of these absorption bands at low temperatures were investigated by Kaiser and Hrostowski.12) According to their results, these absorption bands show characteristic

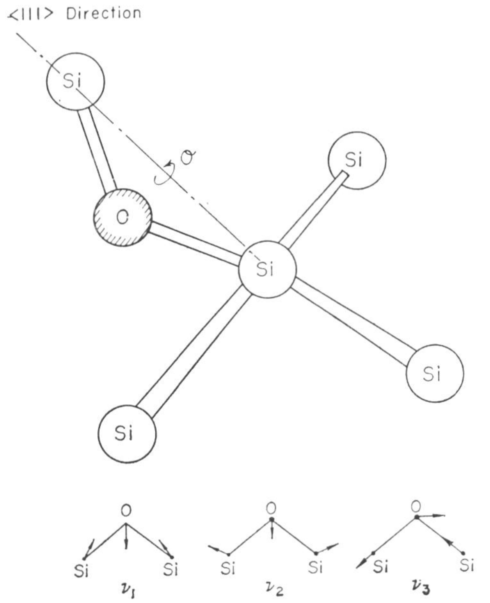


Fig. 1. Structure of O in Si and its vibrational mode.

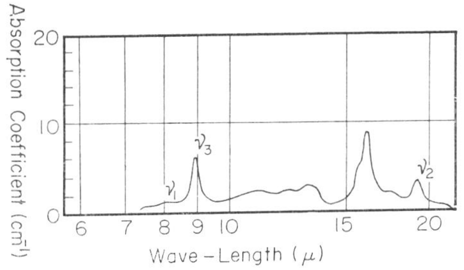
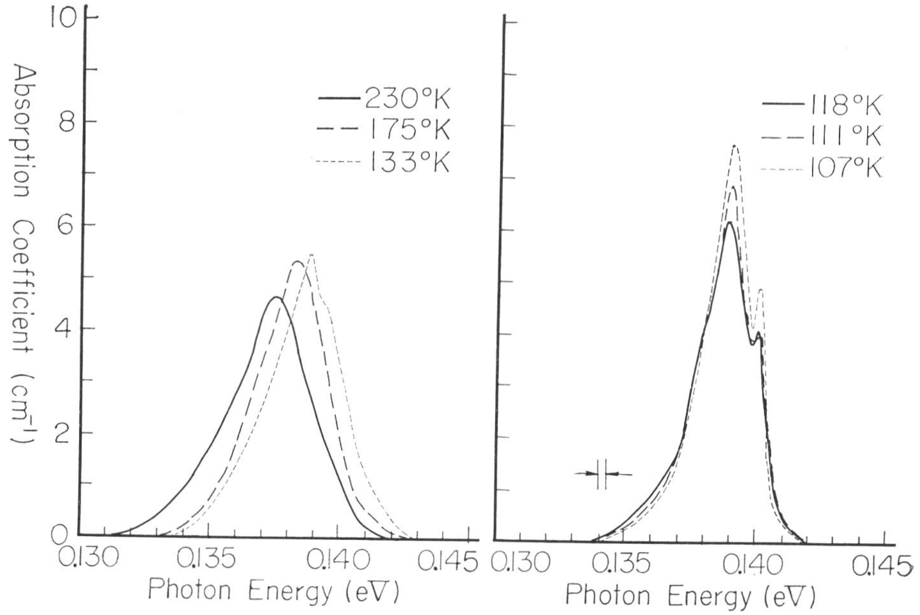
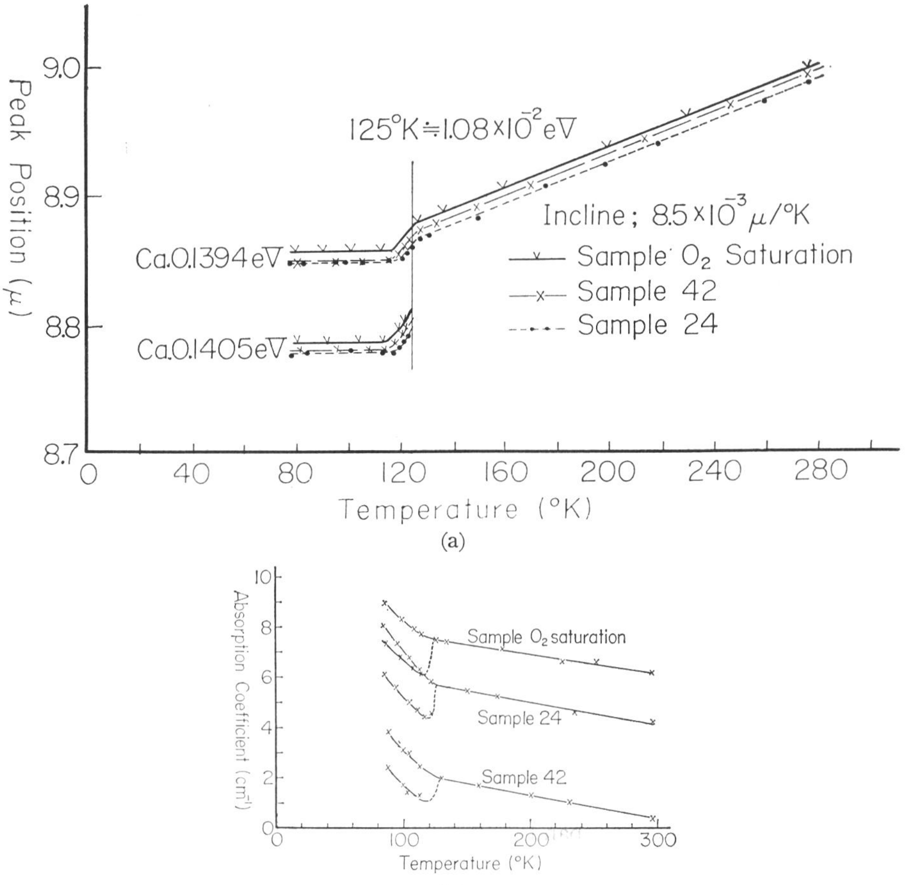


Fig. 2. Absorption spectrum due to O in Si.



a) The higher temperature region b) The low temperature region

Fig. 3. Temperature variation of absorption spectrum at 9 μ.



(a)

(b)

Fig. 4. Temperature variation of peak position (a) and maximum absorption coefficient (b) of 9 μ line.

variations with decreasing temperature. For example, certain absorption peak in these bands split into two at temperatures lower than a certain critical value. The present author have investigated the temperature dependence of 9μ band which is the strongest among these absorption bands, and discussed the reason for characteristic variation and the properties of oxygen defects in silicon crystal.

2. Experiments and Results

All specimens were cut out perpendicular to ⟨111⟩ axis from single crystals which were pulled under various conditions, and were ground to a parallel-sided plate. Then, these pieces were polished optically flat with CeO_2 to the thickness of 2 ± 0.01 mm. The infrared spectrometer used was Perkin-Elmer model 13U-type. The NaCl prism was used. For absorption measurement, the monochromatic light emitted from exit slit of the spectrometer was focused on the samples. The temperature of samples were measured by Cu-constantan thermo-couples. The absorption curves around 9μ are shown for various temperatures in Fig. 3. These curves can be divided into two groups, one being for the higher temperature, and the other for the lower temperature. The critical temperature is *ca.* 125°K, independent on the amount of oxygen contained in the crystal. In the higher temperature region, the peak of absorption band shifts to shorter wavelength with decreasing temperature, and the maximum value of the absorption peak increases with decreasing temperature as shown in Fig. 4 (a) and (b). These variations can be explained by the thermal expansion of the crystal lattice.[12] The right half part of these figures shows the lower temperature effects. The absorption band splits into two peaks, the main peak being fixed. The intensity of main peak lying at longer wavelength side decreases with decreasing temperature, while that of the side peak increases by further cooling. The total absorption area does not change, however, throughout the whole temperature region we measured. The energy of these peak positions are *ca.* 0.1394 eV and *ca.* 0.1405 eV, respectively.

3. Discussion

We shall discuss the low temperature behaviours of absorption curves. It might be reasonable to imagine that the oxygen atom has two types of equilibrium positions around ⟨111⟩ axis in crystal, separated by an energy barrier which is freely jumped over above 125°K (*ca.* 1.1×10^{-2}eV).

The relative population in these two states can be determined by Boltzmann distribution. This energy difference can be determined to be *ca.* 6.0×10^{-3} eV from the temperature variation of intensity ratio. The value of this activation energy varies with samples which were made under different conditions. For example, we observed 1.0×10^{-2} eV for the arsenic doped sample and 9.2×10^{-3} eV for the sample heat-treated for 10 hours at 450°C. There is no relation between the activation energy and the carrier density. For this reason, we can not conclude that any of those energy levels is formed due to the electron trapped by the Si_2O molecule as is the case for the colour center of the ionic crystals. The activation energy has a tendency to decrease with decreasing resistivity. So it may be possible that there is some kind of relation between the density of two energy levels and the imperfections in crystal lattice. The activation energy has a tendency to decrease with increasing dislocation density in the crystal. These situations are shown in Fig. 5. The Si-Si axis of Si_2O molecule lies parallel to the ⟨111⟩ direction. In order to show the validity of such a diagram, we shall consider the variation of potential energy as the function of θ, the rotation angle of oxygen atom around ⟨111⟩ axis. The oxygen atom will, because of the symmetry of the crystal, have six fold rotational symmetry and twelve equivalent position in energy as shown in Fig. 6. Dashed line shows the influence of the nearest Si atoms only, chain line shows the influence of the second nearest Si atoms only, cross-point line shows the influence of the third nearest Si atoms only, and full line shows the total potential energy. There is only one kind of minimum of potential, instead of two as expected from above experiment. However, some kind of internal stress may lift the degeneracy and split up into two kinds of potential minimum with fixed curvatures and varying relative heights with the varying intensity of stress. This idea may be supported by the fact that the activation

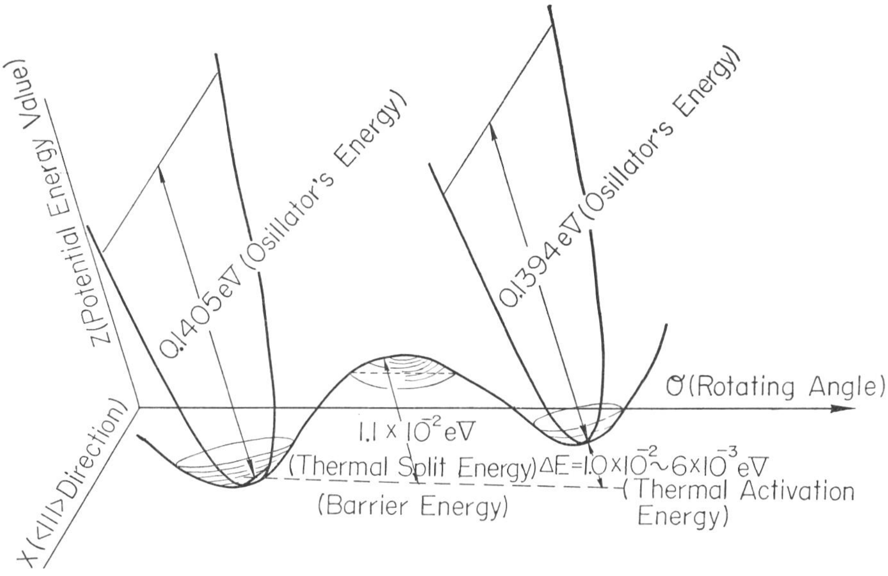


Fig. 5. Potential energy diagram of oxygen as a function of rotating angle θ.

energy is related with the lattice imperfections such as ionized impurity detected by electrical conductivity or the dislocations shown by etch pits. However, this idea is still fairly speculative and further study must be done.

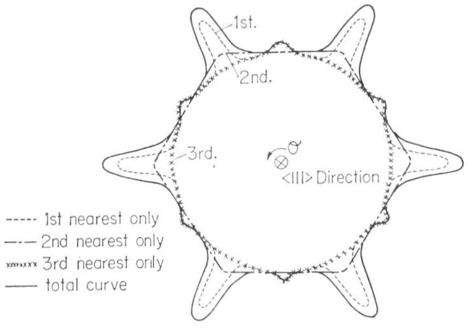


Fig. 6. Calculated potential energy of oxygen as a function of θ.

We can infer that there are some stress around oxygen atoms in the silicon crystals, not only from the above mentioned experimental results, but also from a result of the X-ray microscope.[13] Further, this situation has been also recognized in case of the internal friction measurement of ultrasonic damping due to oxygen atoms in silicon crystals.[13],[14]

Acknowledgement

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DISCUSSION

Balkanski, M.: One would suppose that there is an analogy between the behaviours of the absorption band due to O_2 in Si you observed at 9 microns and the absorption band due to C in Si at 12.2 microns. Your results show two main discrepancies. The absorption coefficient of 9 microns band decreases with increasing temperature, whereas that of 12.2 microns band increases with temperature. On the other hand the 9 micron band shifts to higher energy side with the increasing temperature and the 12.2 micron band moves on the opposite side with a speed of -10^{-5} eV/degree. These discrepancies should be explained on the bases of the differences of the positions and therefore, of vibrations of the oxygen in silicon and carbon on silicon.

Arai, T.: The carbon in silicon occupies the substitutional position, while the oxygen in silicon occupies the interstitial position. The difference of valency between carbon and oxygen suggests that there are some differences of bond natures between them. Furthermore, the thermal expansion coefficient of silicon varies with the amount of oxygen, indicating the existence of some special vibrational mode in this case.

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Mössbauer Effect in Relation to Lattice Defects

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The influences of lattice defects associated with Mössbauer atoms on the Mössbauer emission and absorption spectrum are discussed. Some cases are indicated where information about lattice defects can be obtained with the help of the Mössbauer effect. Two types of defects are distinguished—1) defects resulting from the decay of the parent isotope to the excited state from which the low-energy γ-ray is emitted. They are intrinsically associated with this technique. 2) defects whose association with Mössbauer atoms can be influenced by outside means. The Mössbauer atoms are used here as a probe or tracer. Applying this method, one has to bring a larger part of the Mössbauer atoms close to the defects or *vice versa*. Preliminary results are given for the precipitation processes in an iron-supersaturated Cu-Fe solution using the Mössbauer effect as a tool.

I. Introduction

About 4 years ago, Mössbauer[1)] recognized that a crystal can act similarly to a rigid body insofar as at least a fraction of low energy γ rays are emitted or absorbed in a recoil-free fashion, that is, essentially without energy loss since the crystal as a whole takes up the recoil momentum. Thus recoil-free nuclear γ-rays resonance absorption (Mössbauer Effect) can be observed in solids and also occur in liquids under certain conditions. Small relative velocities between source and absorber (Doppler shift) allow the investigation of these extremely sharp Mössbauer resonance lines. In the case of the transition between the first excited and the ground states of Fe^{57} (transition energy $E_\gamma = 14.4$ kev), the line width, Γ, is about 5×10^{-9} ev and the relative line width is $\Gamma / E_\gamma \simeq 3\times 10^{-13}$.

The Mössbauer effect must be regarded as an extremely valuable scientific tool, especially due to its high relative accuracy. This is manifested in the large number of investigations conducted in the past few years using