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Infrared Absorption Spectra of Defects in Irradiated Silicon*

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Vibrational absorption bands produced in silicon by neutron irradiation and by electron irradiation are studied. The absorption centers involve oxygen atoms in the material. With electron irradiation the production rate of the 11.98 micron band at 80°K is not significantly different from that at 300°K. The result indicates that vacancies are mobile at 80°K with an activation energy for diffusion <0.24 ev. In contrast to the 11.98 micron band, another band at 11.56 microns does not appear under electron irradiation at 80°K but shows up after the sample is warmed to room temperature. Both absorption bands saturate with neutron as well as electron irradiation. Annealing above 473°K produces additional absorption bands in the vicinity of the 11.98 micron band in neutron irradiated samples but not in electron irradiated samples. The additional bands are produced while the 11.98 and the 11.56 micron bands remain unchanged. It is suggested that the centers of the additional bands consist of oxygen atom and defect aggregates.

A series of absorption bands in the range 9–14 microns appear in silicon when it is irradiated with fast electrons or neutrons[1]. These bands are evidently vibrational in nature, as they do not seem to depend on the Fermi level of the sample and also can be observed even at room temperature. The bands sharpen on lowering the temperature of measurement and shift towards shorter wavelengths, the strength of the absorption bands remaining the same. They are found to arise from centers involving dispersed oxygen atoms in silicon, since they are not produced in samples which do not show the 9 micron absorption band of dispersed oxygen, *i.e.* samples from floating zone material and samples from crucible grown material which had been heat treated at 1000°C[2]. The relative strengths of the various absorption bands vary from sample to sample. Moreover, annealing behavior with heat treatment differ for the various bands, indicating that they arise from several independent centers.

The 11.98 micron band, common to all samples studied, has been attributed by Corbett and Watkins[3] to oxygen atoms located each in a vacancy. Fig. 1 shows the flux dependence of this band with neutron irradiation. A very marked saturation effect is observed. Even in the heavily irradiated samples, the 9 micron oxygen band had still more than half of its original strength, indicating that the saturation of the 11.98 micron band was not caused by the exhaustion of dispersed oxygen. It might be suggested that the saturation is the consequence of radiation annealing, *i.e.* irradiation not only produces new centers but also has the effect of destroying the existing centers. However, this explanation requires an unreasonably large cross section for the destruction of the centers. It appears that bombardment produces vacancy sinks, perhaps interstitials, which compete with oxgen for the vacancies.

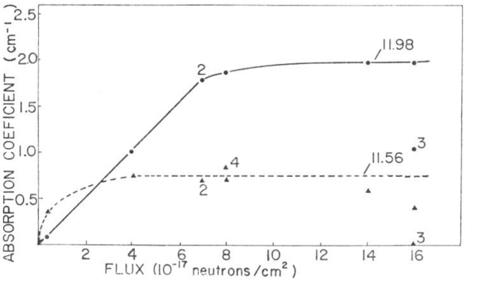

Fig. 1. *Dependence of 11.98 and 11.56 micron bands with neutron flux.* The unmarked points are for samples from one ingot. The marked points 2, 3, 4 are for samples from three other ignots; they are normalized to the same strength of the 9 micron absorption band as that of the unmarked samples. The points 3 seem to be out of line.

Another prominent band, situated at 11.56 microns, is not found in all samples. It appears to involve an additional imperfection besides oxygen. We have not yet been

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successful in the attempt to identify the imperfection. The absorption band was produced with comparable intensities in samples which differed by orders of magnitude in dislocation density, and the band varied strongly in crystals which were grown under apparently identical conditions. Like the 11.98 band, this absorption band also saturates with irradiation. In this case, the saturation may be simply attributed to the exhaustion of the unidentified imperfection.

Since the 11.98 micron band is attributed to a vacancy-oxygen complex, its formation requires the motion of vacancies to oxygen sites. Irradiation with 4.5 Mev electrons was carried out at 80°K and the optical measurements were made with the sample maintained at the low temperature. No appreciable difference in the growth rate of the band was found between the low temperature and room temperature irradiations. The experiment shows that vacancies are quite mobile at 80°K. An upper limit of 0.24 ev is estimated for the activation energy for vacancy diffusion.

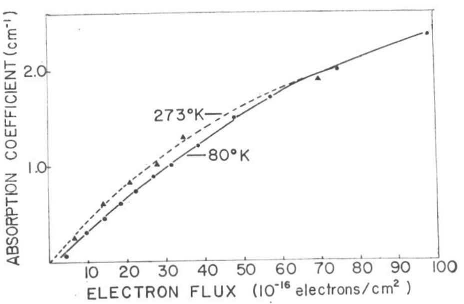

Fig. 2. Flux dependence of 11.98 micron band with 4.5 Mev electrons, the temperatures of irradiation being 80°K and 273°K respectively.

The 11.98 micron absorption band has been identified with a paramagnetic resonance center, A-center, observed in electron irradiated silicon[3]. The resonance center has also been identified with an energy level, 0.16 ev below the conduction band, determined by electrical measurements.[4),5)] The resonance center and the 0.16 ev level were found to be produced at greatly reduced rates at liquid nitrogen temperature as compared to room temperature. Furthermore, warming after low temperature irradiation did not produce nearly the same results as irradiation at room temperature. These results are not consistent with our observation. However, the radiation flux used for the study of the infrared absorption bands is generally much higher than that needed for either the resonance or the electrical measurements. Hence, the results of the resonance and electrical studies may be peculiar to low fluxes rather than indicative of the mobility of vacancies.

The behavior of the 11.56 micron band is quite different. It was absent when the sample was bombarded and maintained at 80°K. After the sample was warmed to room temperature, the absorption band was observed with a strength as if the irradiation had been carried out of 300°K. In view of the closeness in frequency with the 11.98 micron band, it seems likely that a 11.56 micron center consists also of an oxygen atom bonding two silicon atoms on next nearest sites, the shift in frequency being caused by the presence of the additional imperfection. Since vacancies are mobile at this temperature, the above result leads to the assumption that vacancies are trapped near the oxygen-imperfection complex but the formation of the infrared active centers is inhibited at the lower temperature by a potential barrier.

Previous[1)] annealing studies of irradiated samples showed that the centers responsible for the 11.98 and 11.56 bands are stable up to 473°K. Heat treatment studies have been made up to higher temperatures on neutron irradiated samples. Heating at 523°K for 30 minutes produced significant changes in the absorption spectrum (see Fig. 3): (a) Sharp absorption bands, referred to hereafter as satellites, appeared in the vicinity of the 11.98 micron band at 11.88, 12.0, and 12.05 microns respectively. (b) The 11.98 and 11.56 micron bands were left unchanged irrespective of whether the two bands had been saturated during the bombardment. (c) These satellites were observed in samples which showed both the 11.98 and 11.56 bands as well as in a sample which did not exhibit the 11.56 band. Thus the unidentified imperfection of the 11.56 micron center does not seem to be involved. (d) In a sample bombarded with 4.5 Mev electrons, no satellites appeared with annealing up to 573°K even though the sample exhibited the 11.98 and 11.56 bands just as strongly as the neutron bombarded samples. Thus the satellites seem to be peculiar to

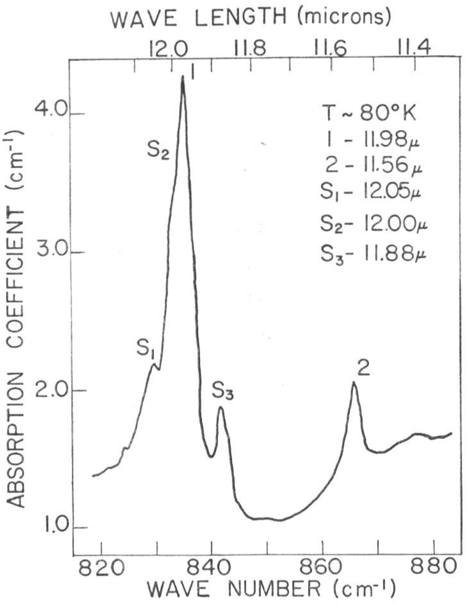

Fig. 3. *Satellites in neutron irradiated silicon after annealing.* Annealing at 523°K for 30 minutes; neutron flux $=12\times10^{17}/cm^2$. 1 and 2 are bands observed before anneal; S_1, S_2, S_3 appear only after the anneal.

neutron damage.

The satellite bands are very close to the 11.98 band, within a range of 12 wave numbers. Like the 11.56 band, but all the more, the satellites appear to arise from the same vibrating units which give the 11.98 band. The slight frequency shifts could be caused by a somewhat different environment. If the effect of the heat treatment required to produce the satellites is to release additional vacancies, then we would expect the 11.98 and 11.56 bands to grow with the satellites, provided the two bands had not been saturated. This is not the case. Furthermore, the satellites do not represent transformations of the 11.98 and 11.56 micron centers, as the latter did not decrease during the heat treatment. The main difference between electron and neutron irradiations is that the electrons produce few secondaries per primary displacement whereas the latter produces a large number of secondaries. The appearance of the satellites in the neutron irradiated sample but not in the electron irradiated sample may be taken as an indication that each center involves more than one simple defect. That the satellites appeared only after heating could be due to the existence of a potential barrier for the transformation of the centers into an infrared active state, as discussed in connection with the 11.56 micron band. Alternatively, the centers might have been formed only at the elevated temperature, an activation energy being required for the elevated temperature, and activation energy being required for the motion of the defect aggregates from which the centers are formed. For example, such defect aggregates may be divacancies.

An interesting behavior was observed on two relatively weak bands, at 10.35 and 10.42 microns, in neutron irradiated silicon. Upon annealing at 200°C, two new bands appeared, one on either side of the original pair, while the original bands decreased in intensity and finally disappeared, as shown in Fig. 4.

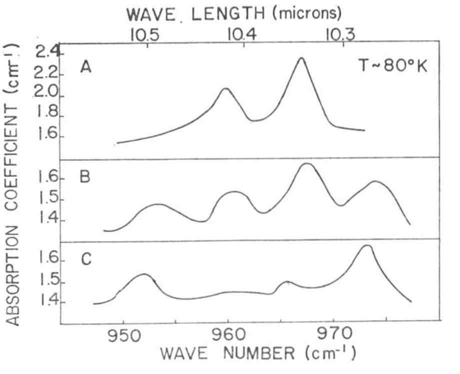

Fig. 4. *Transformation of 10.35 and 10.42 micron bands in neutron irradiated silicon, due to annealing.* Neutron flux $=8\times10^{17}/cm^2$. A) Before annealing. B) After 30 minutes at 473°K. C) After 90 minutes at 473°K.

The new bands, at 10.98 and 10.50 microns, have an average frequency the same as that of the two original bands. The behavior is suggestive of that of two coupled oscillators with a frequency split by the coupling, the effect of annealing being a closer coupling of the two oscillators.

We would like to thank Prof. J. W. MacKay for the electron irradiations and Dr. J. H. Crawford and Dr. J. W. Cleland for the neutron irradiations.

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DISCUSSION

Elbaum, C: I wonder why it is necessary to assume that the vacancy migrates, rather than a trapping defect, in view of the surprisingly small migration energy observed, both by the authors and by Dr. Watkins.

Ramdas, A. K.: There is no doubt that the defect responsible for the observed facts is the vacancy. It is possible that other migration mechanisms (not simple vacancy migration) are involved, but these would have to be very complex, however one must keep an open mind on this problem.

Watkins, G. D.: First let me make a comment to Prof. Elbaum's question. In addition to vacancy-oxygen pairing, we also observed vacancy-phosphorous pairing. The vacancy is thus the common denominator suggesting that *it* is the mobile entity. Also, as discussed in my paper, we see vacancy-vacancy pairing to form divacancy. Taken together, these give strong evidence for the motion of the *vacancy*.

Second, let me make a comment to the paper of Ramdas and Fan. I agree with your comment in which you suggest that we must keep an open mind as to the mechanism by which the 11.98 band (A-center) is produced. As is mentioned briefly in the version of my paper, we have also studied the emergence of A centers (and E-centers) in n-type silicon upon annealing after low temperature irradiation. We find that the centers emerge in two discrete temperature regions, one of which is at a much lower temperature than that at which the vacancy is observed to disappear in p-type silicon. It is thus possible that more than one mechanism is operative for the defect formation. Further study must be done to determine whether the low temperature process is associated which the long range diffusion of the vacancy or whether there is some process by which there is preferential vacancy formation in the vicinities of oxygen and the phosphorous atoms. As you say, an "open mind" is necessary. I think that the experiments in p-type silicon which I described in my paper give strong evidence for vacancy motion. However, there may *also* be other mechanisms for A and E center formation as is evidenced by the complex emergence behaviors of the centers, as well as your observations of A center production rates at 80°K.

Fan, H. Y.: In regard to Dr. Watkins's suggestion, that Si-A center may be formed by one process at low temperature about 90°K and by some other process at higher temperature, I wish to stress our observation that 11.98 band is formed at the same rate with electron bombardment at 80°K and 273°K.

My second comment is: there is some discrepancy between the vacancy motion as deduced from Watkins's "single vacancy" spin center studies and that indicated by our 11.98 band production by bombardment at 80°K. According to Watkins's result, it would be very difficult to produce the 11.98 band at 80°K. More studies are needed to obtain complete understanding.

My third comment: Beside the satellite bands produced near 11.98 microns by annealing, difference in the effect of electron irradiation and neutron has been found in the production of 1.8 micron band, as reported by us in Prague.