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Final Report
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INFRARED ABSORPTION DUE TO IMPURITIES AND
RADIATION DAMAGE IN SEMICONDUCTORS

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Introduction

Shallow donor and acceptor states in silicon and germanium have been the subject of considerable interest and effort, both experimental and theoretical. The first work in this area was devoted to the study of states due to substitutional impurities (of atoms from groups III and V of the periodic table), and both experiment and theory have been reviewed by Kohn (1). The experiments have consisted of infrared absorption measurements on samples containing small amounts of the impurity (usually 10^{15} to 10^{17} atoms/cm³). The small concentration is necessary to avoid overlapping wave functions due to states of neighboring impurities. Also the sample must be refrigerated (usually to liquid helium temperature) so that a large fraction of the donors or acceptors will be un-ionized. The absorption spectra thus obtained give the energies of the excited states of the impurities, as well as transition probabilities and ionization energies.

More recent work has extended this type of measurement to other impurities. At this laboratory we have investigated lithium and lithium-oxygen complexes in silicon (2), the most recent of this work being supported by NASA and described below. These optical measurements have also been used in studies of defects introduced in radiation damage of semiconductors. To date, the defects which have been observed by this method have all involved an impurity as an integral part of the defect (3). The efforts and results of our study in this area are described below.

This report, then, describes the optical measurements conducted over the last three years and consisting of the study of several types of defects in silicon. The work can be conveniently divided into the following parts:

- (I) The lithium-oxygen interaction in silicon has been the object of considerable further examination, extending the work previously done at this laboratory (2).
- (II) Electron-irradiated silicon has been studied. Several samples and different approaches have been used including helium temperature irradiation.

(III) The L-center, presumably a lithium-damage-center complex in silicon, has been noted in electron paramagnetic resonance measurements (4). The third phase of our work has sought possible optical absorptions due to this L-center.

I. Lithium in Silicon

The previous work at this laboratory (2) on lithium in silicon had been carried out on silicon crystals which were either float-zone (FZ) prepared or pulled from quartz crucibles (QC). The former have low oxygen concentrations while the latter have oxygen concentrations of the order of 10^{17} to 10^{18} cm^{-3} and higher. Just how low the oxygen concentration is in FZ samples, (and how much it varies) has not been directly determined due to several experimental difficulties. Use of the nine micron absorption below concentrations of 10^{17} cm^{-3} is difficult if not impossible. A direct determination by mass spectroscopy for these levels is complicated by surface oxide layers.

Notwithstanding these difficulties it is important for several reasons to know the behavior of oxygen in silicon when the concentrations might lie in the range from 10^{14} to 10^{17} cm^{-3} . Accordingly, one direction of the present research as previously indicated has been the study of the Li-O interaction in this oxygen concentration range, i.e., in the range between "typical" float-zone and "typical" Czochralski quartz crucible silicon. Since oxygen concentration determination is so difficult, it was determined to use the experiment to give an indication of oxygen concentration, i.e., to look for samples which gave both the typical FZ infrared spectrum for lithium (interpreted as due to the isolated lithium atom), and the QC lithium spectrum, which is apparently due to LiO.

Three equations may be written down which involve the lithium concentration, $[\text{Li}^+]$, the lithium oxide concentration $[\text{LiO}^+]$, and the oxygen concentration,

[O].

$$[\text{LiO}^+]\text{C} = [\text{Li}^+][\text{O}],$$

$$[\text{O}] + [\text{LiO}^+] = N_{\text{O}},$$

$$[\text{Li}^+] + [\text{LiO}^+] = N_{\text{L}}.$$

Here N_{O} is the total number of oxygen atoms per cubic centimeter and N_{L} is the total number of lithium atoms per cubic centimeter as determined by room temperature resistivity measurements. The room temperature equilibrium concentration values are found using the room temperature values of C which equals 10^{15} cm^{-3} (5). These concentration values are assumed to be the values seen during a low temperature experiment (i.e., the room temperature values are "frozen in").

From the above considerations it is inferred that FZ crystals have an oxygen concentration of 10^{14} cm^{-3} or less since no LiO spectra have yet been positively detected in FZ crystals. That is, it is inferred that with the range of $[\text{Li}^+]$ used, an N_{O} of 10^{14} cm^{-3} is probably detectable, and an $N_{\text{O}} = 10^{15} \text{ cm}^{-3}$ would give an LiO spectrum which would be clearly discernible.

Two samples which we have studied in this program came from a crystal which was first grown by the Czochralski method from a quartz crucible and then had one pass made through it by a floatzone in vacuum. The sample was n-type before lithium diffusion, having been doped with phosphorus to a concentration of 10^{15} cm^{-3} as indicated by room temperature resistivity. The nine micron absorption showed no detectable oxygen. The absorption spectrum is given in Figure 1. The second of the samples had a somewhat high donor concentration, but showed a similar absorption spectrum. The spectrum indicated a split in the phosphorus peaks normally occurring at 34.4 meV ($2P_{\text{O}}$), and 39.2 meV ($2P^{\pm}$). The split in these peaks was observed to be 0.8 ± 0.1 meV. These peaks do exhibit a similar splitting when subjected to uniaxial stress. Thus further experiments

were performed to determine if a new effect was being observed. Samples containing phosphorus in this same concentration range were obtained from another supplier. Similar absorption spectra were run, and no splitting was found. A re-run on the first sample was then made, and this time no splitting was observed for the phosphorus lines in it. It is thus concluded that the first holder exerted a stress on this sample the first time, and that the splitting was due to this stress.

In order to observe unambiguous spectra from both isolated lithium and lithium oxide in the same sample, it would be necessary to obtain silicon with an oxygen concentration of about 10^{15} /cc. Single crystal silicon with this oxygen concentration is not readily available. It could probably be prepared by introducing oxygen into the furnace while a silicon boule is being zone refined. To develop the technique needed for this process would no doubt require extensive experimentation on the part of the supplier. It has not been possible to conduct such a study and the sought for sample showing both Li and LiO absorptions has not been obtained.

The results of this phase of the research have served to provide further information on the behavior of oxygen in silicon. In the sample referred to above, a single zone pass of a crystal first pulled from a quartz crucible has shown no evidence of the LiO spectrum and thus suggests that the oxygen has diffused from the crystal. It is, of course, possible that the oxygen has not left the crystal but formed some sort of aggregates which do not show. This is thought to be less likely, however, since the results of reference 2 indicate that lithium-oxygen complexes of higher oxygen ratios do show an infrared absorption spectrum in the range covered. When taken with Pell's results (5), the indication is that the single zone pass has reduced the concentration to something of the order of 10^{14} cm⁻³.

II. Low Temperature Electron Irradiation and Infrared Study

In spite of the large amount of information which has been obtained on defects in irradiated silicon there is little of these data which do not depend fundamentally on a particular impurity which is an essential part of the defect (see Ref. 3). For example, electrons paramagnetic resonance (epr) spectra have been attributed to vacancy + phosphorus, vacancy + aluminum, vacancy + oxygen, interstitial aluminum + substitutional aluminum, etc. In the only instance of the observation of an isolated primary defect two epr spectra have been attributed to the isolated vacancy in two different charge states. In the case of the interstitial silicon atom which must be formed in each primary radiation damage event, no data is observed which can be attributed to the isolated defect. Indeed, the fate of the interstitial atoms was a complete mystery until recent work by Watkins (see Ref. 3, pg. 78). This work has served to emphasize the extremely mobile nature of these interstitials even at temperatures below 80°K, and has involved an impurity atom (aluminum in this case) in the observable defect.

Thus it was determined to attempt observation of some of these mobile defects by irradiation in a cryostat which allows for the irradiation to be carried out at low temperature, and the study (in this case infrared absorption) to be carried out without breaking vacuum or allowing the samples to warm up.

The V.P.I. 1.5 Mev Van de Graaff accelerator was modified to produce electrons, and a number of experiments have been carried out. High resistivity (500 ohm-cm) P-type silicon was first bombarded at liquid air and liquid helium temperatures with about 2×10^{16} electrons cm^{-2} at an energy of 0.7 Mev. The absorptions which were observed and reported in the last two semi-annual reports have now been determined to be spurious. They do not appear where the sample chamber is separated from the beam tube by a 1 mil aluminum foil, and are apparently due to the deposit on the cold sample of organic fragments produced by the ionizing radiation.

With the aluminum foil in place, irradiations with as many as 0.4×10^{17} electrons cm^{-2} at an energy of 0.7 Mev have been carried out at liquid helium temperatures (T about 12° K.). The entire wavelength range from 2 - 35 microns was then covered, and no new absorptions found in any part of the range. This higher irradiation thus gives the same results as those carried out earlier and reported in the last two semi-annual reports when allowance is made for the spurious absorptions.

The results which have been obtained in this phase of the research constitute important corroborative evidence for the mobility in silicon of interstitials at very low temperatures. Electron spin resonance experiments had indicated by indirect results that interstitials were mobile at temperatures as low as 4° K. But there are defects in silicon (e.g., the isolated lithium impurity) which do not give an esr signal and do give rise to infrared absorption. The results of this phase of our observations, with irradiation at temperatures as low as 12° K, give further evidence that the interstitial does not remain even at this very low temperature. One possibility, however, should be pointed out: it is distinctly possible that the interstitial, or the vacancy-interstitial pair, may undergo radiation annealing due to the infrared radiations falling on the sample in the absorption determination. There has been considerable evidence recently of radiation annealing, and this possibility should not be overlooked.

III. Attempt To Observe Optical Absorption By the L-Center

A number of attempts to induce an optical absorption which would be attributable to the lithium-damage-center complex (4) in silicon have all been unsuccessful. Initial resistivity and irradiation times were first chosen to correspond closely with those used by Goldstein, as this appeared to give the best probability of producing an observable absorption. Then variations were made in these parameters, but still no optical absorptions were found.

The first sample had been doped with lithium by the usual lithium diffusion technique, i.e. from a lithium-tin bath. The resultant resistivity (0.15 ohm-cm) indicates about 5×10^{16} lithium atoms per cubic centimeter. The sample was irradiated with a total flux of 3.4×10^{16} electrons of 0.5 to 0.6 Mev energy. This corresponds to 0.7×10^{15} electrons per square centimeter. Another sample was lithium-doped to a concentration of about 5×10^{15} atoms/cm³ and irradiated with 1.0×10^{16} electrons/cm². In this case the electron energy was 0.7 to 0.8 Mev.

This last sample was again irradiated with approximately the same total flux as before so that the total amount received was 2.1×10^{16} electrons/cm². In all of these cases, as was indicated above, no indication of induced optical activity could be found.

It is perhaps appropriate to report that subsequent experiments on electron irradiation of phosphorus-doped silicon by the same electron source have produced previously reported damage centers. These centers have been studied by resistivity and annealing experiments, and have also given rise to optical absorption.

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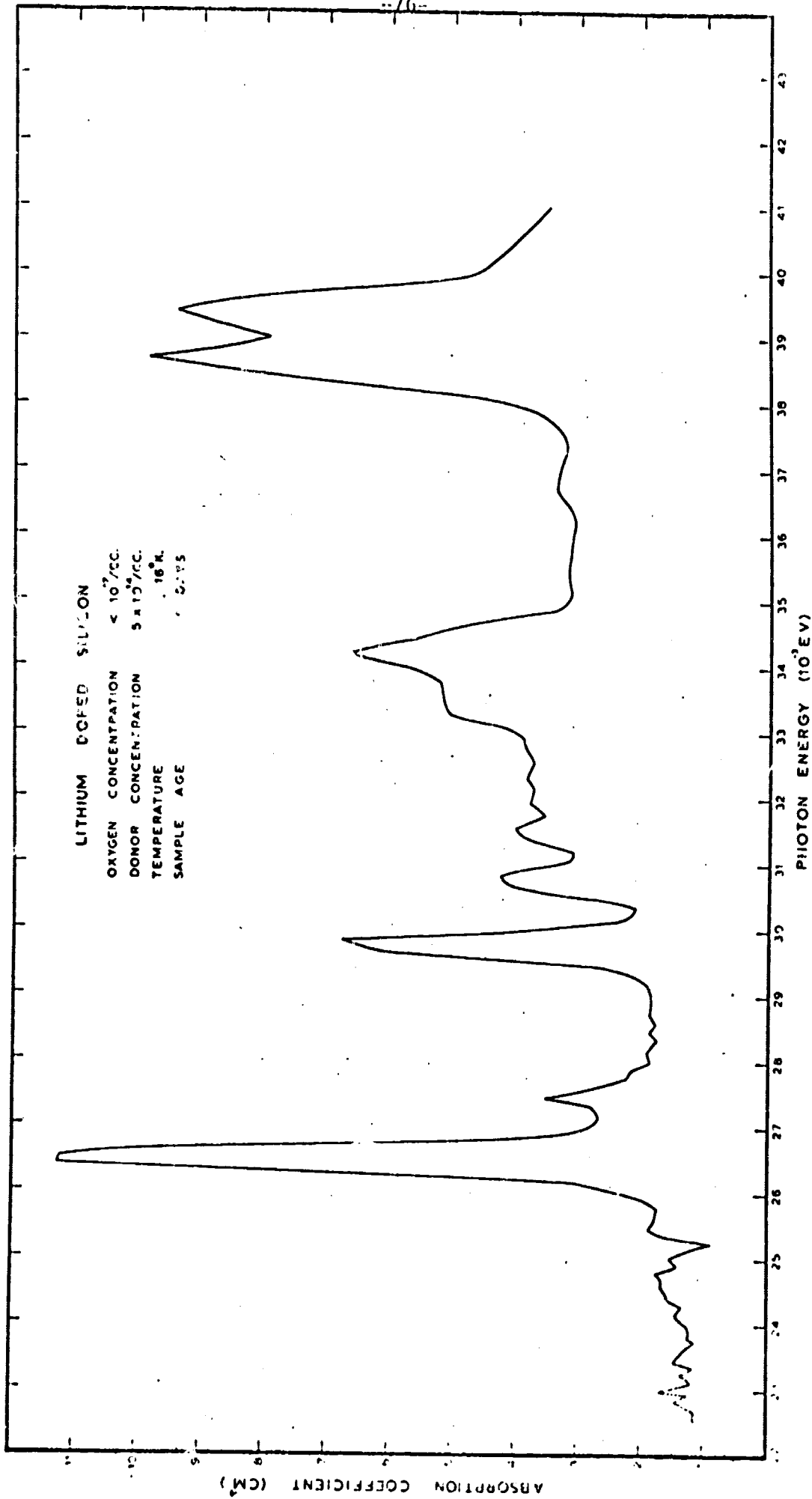


FIGURE 1 ABSORPTION SPECTRUM OF SILICON SAMPLE NASA-1